UNIVERSITY OF BIRMINGHAM

LIFE CYCLE ANALYSIS OF BIOMASS DERIVED FUELS FOR FUEL CELLS

By

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HYDROGEN, FUEL CELLS & THEIR APPLICATIONS WITH INTEGRATED STUDY

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DECLARATION

I, Sophie Alice Archer, hereby declare that the work presented in this thesis is my own with no help of more than the cited literature and auxiliary editorial feedback from Professor Richard J. Murphy (University of Surrey), Dr Andrew Ingram (University of Birmingham), and from my supervisor, Professor Robert Steinberger-Wilckens for published content produced as a result of the research conducted for this thesis (co-authorship purposes only).

I also confirm that this work has not been submitted to another examination office, neither in content nor in shape.

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Signature (Sophie Alice Archer)

Date: _____

ABSTRACT

The core purpose of this thesis was to identify and assess alternative sources of fuel gases for use in fuel cells and demonstrate their environmental impact in comparison to fossil fuel reference cases. By utilising biomass, fuel gases were found to be sourced from several feedstocks, including biowastes. The chosen methodology for achieving this purpose, was Life Cycle Analysis (LCA). Through the exploration of LCA methodologies and gaining new understanding of the varieties of techniques available, the guidance provided by the ISO standards (ISO 14040 and 14044) established a core four-stage method that all LCA practitioners must abide by to be consistent. ISO 14025 provides in-depth guidance for comparative LCAs.

Concerning advancements in biomass conversion techniques, three core biomass generations can provide a multitude of gaseous and liquid fuel products from a variety of feedstocks. In order to produce an LCA for gaseous fuels from biomass, a novel synthesis of primary data, using the baseline chemical composition of inputs and outputs, alongside process efficiencies and gas clean-up technologies was required. All gaseous biomass pathways identified were established alongside fossil derived reference cases. In addition, an overview of different types of fuel cells, a technology that converts a fuel gas (e.g. hydrogen) to electricity electrochemically is presented.

Finally, the conduction of a comparative LCA of viable biomass pathways produced a multitude of results, across a number of assessments. The key findings of this thesis include the insight that even pathways with low efficiency and high fuel gas demands have the potential for low ecological impacts, as metabolic processing has some of the lowest process efficiencies due to biological limitations, whilst also producing high yields of gas per kg of biomass feedstock (in this case, algae). Fuels derived from biomass were found to be highly ecologically competitive against fossil fuel reference cases, with third generation algal pathways and second generation biowastes utilised in SCWG, being the most favourable, followed by anaerobic digestion. SOFCs also proved to be a more favourable technology than PEFCs, due to their wide range of fuel choices and higher efficiency.

DEDICATION

In memoriam: My Grandad, Clive Easton

A Good Man

14th February 1933 – 23rd November 2007

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To my supervisor: *Professor Robert Steinberger-Wilckens*. Thank you for all your patience and understanding throughout these years. Your assistance and diligence have helped me explore my potential and I am most appreciative of all your help. It has been a pleasure to have been able to complete this project under your supervision.

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LIST OF ABBREVIATIONS

Abbreviation	Definition
AFC	Alkaline Fuel Cell
BD	Biodiesel
BM	Biomethane (from Biogas)
CCS	Carbon Capture and Storage
CFD	Chemical Feedstock Demand
CHP	Combined Heat and Power
CPE	Conversion Process Efficiency
CPO	Crude Palm Oil
CRPE	Clean-up / Reforming Process Efficiency
DEFRA	Department of Environment, Food and Rural Affairs
EFB	Empty Fruit Bunches
F^{ar} / F^{daf}	Feedstock, as received / dry and ash free
FFB	Fresh Fruit Bunches
FCO	Feedstock to Fuel Efficiency
FCE	Fuel Cell Efficiency
FGD	Fuel Gas Demand
FU	Functional Unit
GWP^{100a}	Global Warming Potential over 100 years
GHG	Greenhouse Gas(es)
GREET	Greenhouse Gases, Regulated Emissions and Energy use in Transport
IGCC	Integrated Gasification Combined Cycle
IPCC	Intergovernmental Panel on Climate Change
LCA	Life Cycle Analysis
LCI	Life Cycle Inventory
LHV	Lower Heating Value
MCFC	Molten Carbonate Fuel Cell
NG	Natural Gas
NREL	National Renewable Energy Laboratory
PAFC	Phosphoric Acid Fuel Cell
POBD	Palm Oil Biodiesel
POME	Palm Oil Mill Effluent
PEFC	Polymer Electrolyte Fuel Cell
PgC	Petagram's of Carbon
PSA	Pressure Swing Adsorption
RGD	Raw Gas Demand
RTFC	Renewable Transport Fuels Certificate
RTFO	Renewable Transport Fuels Obligation
SCWG	Supercritical Water Gasification
SG	Syngas
SOFC	Solid Oxide Fuel Cell
TRACI	Tool for the Reduction and Assessment of Chemical and Other Environmental Impacts
WCED	World Commission on Environment and Development
WGS	Water Gas Shift
UN	United Nations
UNFCCC	United Nations Framework Conversion on Climate Change

CHAPTER 1

CHAPTER 1. INTRODUCTION

1.1. The Challenge of Climate Change

Resource depletion is an ever-increasing concern for modern society. Since the industrial revolution and the discovery of fossil fuels, the amount of carbon dioxide emissions slowly increased between 1850 and 1900 (from ~0.2 Petagrams of Carbon per year (PgC/year) to ~1.3 PgC/year), with heightened emissions occurring between 1900 and 1950 (from ~1.3 PgC/year up to ~2.7 PgC/year) [1] as manufacturing and use of motor vehicles increased (especially during the first and second world wars - cars, tanks, planes). The highest levels of increase occurred from 1950 to present day, due to worldwide GDP growth and the growing popularity of owning motor cars [2], for which the emissions increased from ~2.5 PgC/year to 10 PgC/year in 2011 (*Figure 1.1*) [1].

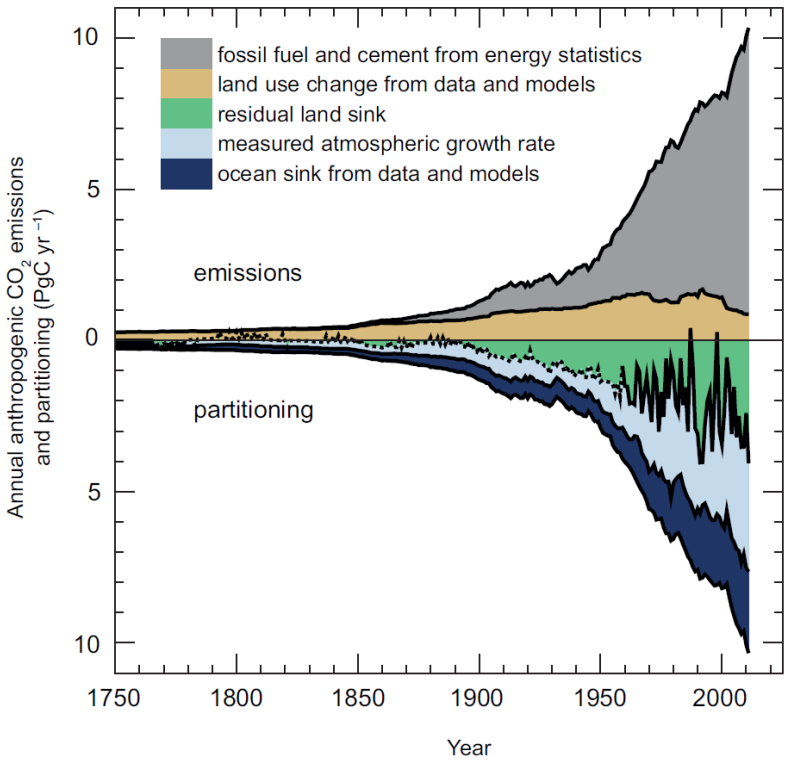

Figure 1.1: Annual anthropogenic carbon dioxide emissions and their partitioning among the atmosphere, land, and ocean from 1750 to 2011

Source: IPCC Fifth Assessment Report 2013 (reports figures directly taken are permitted for non-profit use) [1]

For perspective, 1 Petagram of Carbon = 3.67 gigatonnes of carbon dioxide [3]

Carbon dioxide is released into the atmosphere, but only some emissions remain there. The majority of emissions are absorbed by ocean and land carbon sinks [1, 4], whether it be the carbon dioxide is precipitated out of the atmosphere or fixed by plants. On a whole, the average global temperatures are on the rise [4-6] and when this data is mapped across the earth, the majority of warming is found in the northern hemisphere, especially towards Siberia and the Arctic (*Figure 1.2*) [7].

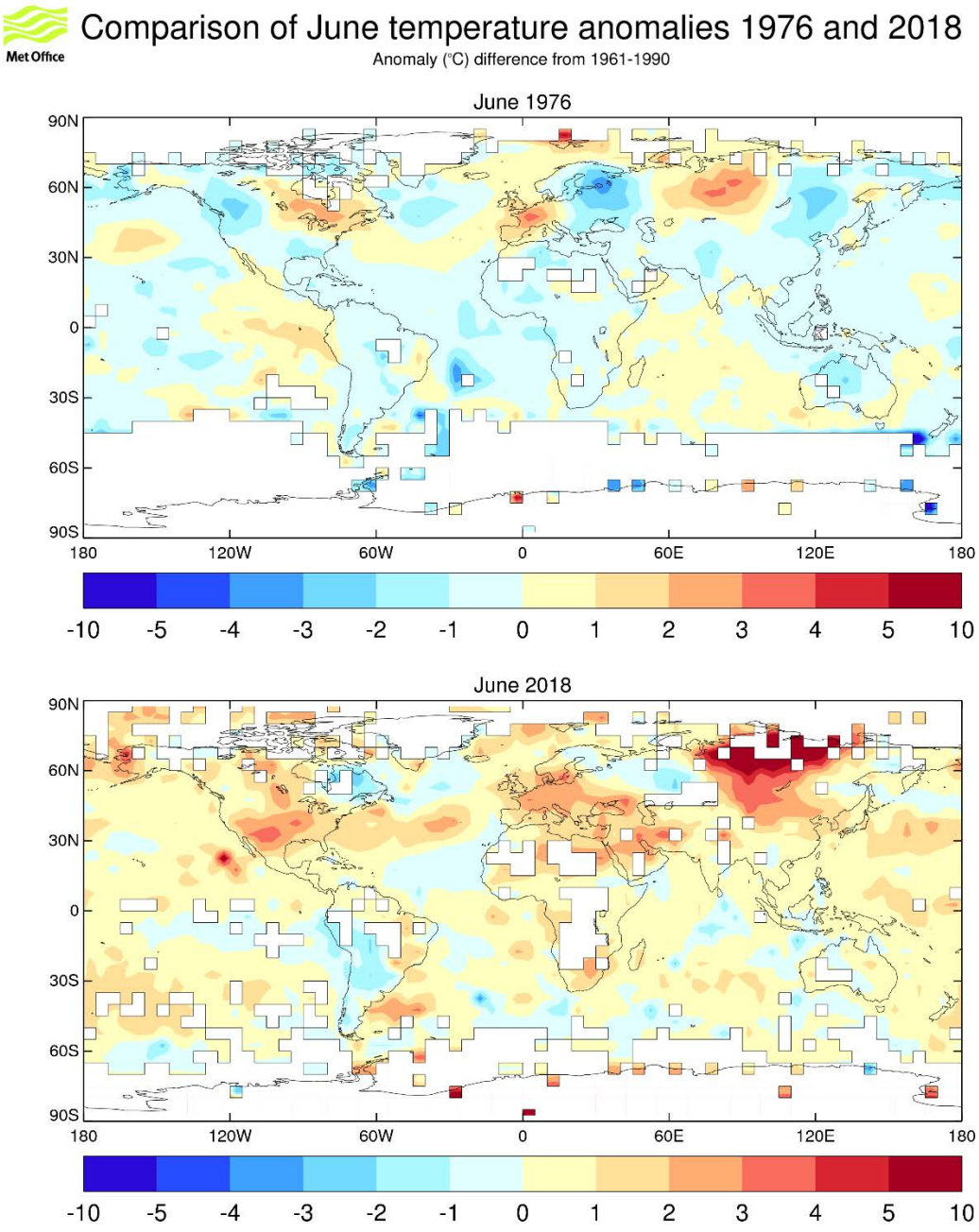

Figure 1.2: Surface Temperature Anomalies from 1976-2018 - June average

Source: [7]

Some citizens around the world are sceptical about whether temperatures are increasing; feelings which are usually exacerbated after a freak local snowfall, flooding or drought. What is not understood, though, is the statistical nature of global temperature increase. This does not exclude that regions become colder on average as others heat up (*as seen in Figure 1.2 with the general warming across the globe since 1976, with exceptions of eastern Canada, where it shows a decrease in temperatures*). Temperature influences the very basic principles of weather and climate on earth.

The speculation of 'global warming is going to make things hotter' is simplistic in that variations in temperature effect the frequency and amplitude of climate irregularities, for instance augmented storms and snowfall, which occur as regularly as heat waves. One thing that is definitely irregular is the increasing level of greenhouse gases (GHGs) and alterations of polar temperatures [1, 8]. However, these in themselves are another misconception. People believe that as carbon dioxide increases, temperature, ice melt, and oceanic acidity increase, too, but there is a lag between all of these things, so the initial impact of one thing does not show immediately [9-11]. Therefore, the true extent of how impacts from present actions are going to affect future generations is unknown.

1.1.1. International Recognition and the Earth Summits

In 1972, the United Nations (UN) held the 'UN Conference on the Human Environment' (Stockholm Earth Summit) and established the UN Environment Programme (now known as UN Environment [12]). However, the 1972 and 1982 UN earth summits received little political interest due to growing concerns about the cold war [13]. Determined to encourage international engagement, they established the Intergovernmental Panel on Climate Change (IPCC) in 1988, together with the World Meteorological Organization. This was also spurred as a result of the World Commission on Environment and Development

(WCED) publishing the Brundtland Report - 'Our Common Future' [14] a year earlier in 1987.

The WCED created the Brundtland Report to highlight the environmental, social, and economic threats (later adopted by the IPCC) that came with the world's current unsustainable and unequal development across richer and poorer countries [14, 15]. The term sustainable development was introduced, meaning 'meeting the needs of the present without compromising the needs of the future' [14], which urged an international agenda for change through united development strategies.

Encouraged by the Brundtland Report and IPCC's First Assessment Report (1990), the UN General Assembly organised the 1992 Earth Summit in Rio de Janerio, Brazil, titled 'the UN Conference on Environment and Development' [16]. The historic success of this summit created an unprecedented global strategy for sustainable development - 'Agenda 21', which more than 178 governments voted to adopt [13, 17] in tackling poverty, creating sustainable population levels, and protecting the environment through biodiversity conservation and pollution regulation [13, 18]; however, this strategy was not a legally binding set of principles. Here, in 1992, the 'UN Framework Conversion on Climate Change' (UNFCCC) was opened to the attending governments [19] and came into force in 1994 with 196 parties [20]. Its purpose was to limit greenhouse gas emissions to a level that would not cause dangerous alternations within the future climate – this being the driver for the Kyoto Protocol and the Paris Agreement (*Section 1.1.2*). The Berlin Mandate established the negotiations running up to the Kyoto Protocol, which were also included in the IPCC Second Assessment report that was delivered in 1995, to aid in its adoption [21].

In 2002, Johannesburg hosted the World Summit on Sustainable Development. It was seen as one of the largest international gatherings for the subject [22]. Its aim was to identify

quantifiable targets and cement international commitment to Agenda 21, which so far had yielded little commitment due to its non-binding status [23, 24]. The Summit, originally hopeful of progress, resulted in failure. Governments were not able to be held accountable to their lack of commitment, and failed to agree on meaningful, time-bound actions for future progress [25, 26]. The outcomes of this Summit (and also that of the Copenhagen G8 Summit in 2009) were found to be but a reiteration of previous years, further demonstrating the loss of momentum that Rio 1992 had originally inspired [25, 27].

The UN Conference on Sustainable Development took place in 2012, back in Rio (also known as Rio+20) attempting to rekindle the lost passion of the sustainable development and environmental movements. Its reception was one of the largest UN conferences yet, bigger than the original Rio 1992 Summit, but the expectations for change fell short as (once again) commitments failed to be enforced by government leaderships [28, 29]. However, the private sector stepped up and actively engaged in the initiative proposals, helping to produce the outcome document 'The Future We Want' and providing some hope for future progress [28-30]. This further led to the 'Transforming Our World' agenda in 2015, which will continue sustainable development plans to 2030 [31].

1.1.2. The Kyoto Protocol and Paris Agreement

From 1992 to 2004, the UNFCCC parties convened to determine specific targets for GHG emissions in an endeavour to reduce them by 2012 (Rio +20). The chosen emissions include carbon dioxide, methane, sulphur hexafluoride, and nitrous oxide, in addition to fluorocarbons [32, 33]. In February 2005, 'The Kyoto Protocol' was brought into effect; an international treaty for which governments are bound to commitments of emission reductions between 2008 and 2012 (the first period) [34]. Depending on each country's current emissions, varying targets were allocated i.e. high pollutant emissions, high targets,

which resulted in increases in international emissions trading and therefore, for some countries, no reductions were made. In prosecution of this, governments unable to achieve their targets in the first period had to rectify their emissions before the end of the second period (2012-2020 under the Doha Amendment), without the use of emissions trading [35].

In 2011, the UFCCC came to the agreement that legally binding measures must be implemented from 2020, for real change to occur. This led to the Paris Agreement in 2016, where 195 parties (both developed and developing alike) signed in consensus to strengthen global response to climate change, sustainable development, and eradication of poverty [36, 37].

Overall, the Paris Agreement is much like every other UN agreement since Rio 1992, recognising the need for: advancing research to determine the true threat of climate change; assistance of vulnerable developing countries in climate adaptation through resources and finance from public and private sectors, and sharing of technologies; and safeguarding food, water, and the integrity of all ecosystems [36]. Its core objective is to prevent temperature increases above 2°C and pursue efforts of limiting temperature increase to 1.5°C [36, 38], as discussed in Copenhagen (December 2009) [39] and the Republic of Korea (October 2018) [38], although there are reservations about this radical ambition and the length of time required to release it, especially taking into account the exit of the USA [40-43]. Further meetings took place in Bangkok (September 2018) and Katowice (December 2018) to revise agendas and articles within the Paris Agreement [44]. The IPCC Sixth Assessment Report is expected to be finalised between 2019 and 2022, with reflection on the Paris Agreement.

1.1.3. Recent UK Political Developments

In response to the ever growing threat, governing bodies across the world have become more active regarding climate change and climate adaptation policies. In the UK, the '2008 Climate Change Act' was introduced by the Department of Environment, Food and Rural Affairs (DEFRA) to provide political support for further development and increase evidence through research opportunities for climate issues and how the UK will adapt to future threats [45, 46]. The 'Climate Change Risk Assessment' was put into place in 2012, with requirements to update it every 5 years, alongside publishing evidence reports to show its progress [47]; the next update is due in 2022.

In 2009, the European Commission released a White Paper concerning an action plan for a European Framework towards adaption to climate change [48], which the UK adopted. It discusses why climate change is an issue that needs to be addressed, focusing on the issues brought by land and sea temperature changes, precipitation changes, and sea level changes, as well as their impacts on food and water. As GHG emissions are the leading causes of climate change, whether it be from energy, transport, or agriculture, finding alternative fuels (such as biodiesel and biofuels) and introducing sustainable, cleaner technologies (such as renewable energy technologies and fuel cells) is of growing importance.

The action plan White Paper led to the 'EU Strategy on Adaptation to Climate Change' in 2013. It was stressed that no matter how much is done to mitigate, there will still be requirements to plan for adaption - essentially the need of 'Climate Proofing' [49]. According to this report, areas of adaption that require focus consist of, but are not limited to: flood planning; water management systems; early warning systems; ecosystem management; and construction and infrastructure resilience, in response to the

requirements of adaption plans. Addressing resource depletion and energy use are further areas of great significance, which further emphasised the driving points in the action plan White Paper, reducing the impact of climate change as much as possible. The UK responded to this with its second instalment of the 'Climate Change Risk Assessment' in 2017 [50]. Within this, flooding, public water supply, biodiversity, and temperature changes were at focus, as well as prioritising further research and government policies and activities for the above topics, and promoting clean business and industry showcases [50].

The UK's 'Clean Growth Strategy' was published in 2017 [51], having successfully achieved over 40% GHG reductions from 1990 levels. A further 40% emission reductions are hope to be achieved by 2050, totalling an 80% overall reduction [51]. An update was released by DEFRA in July 2018 as part of the 'National Adaptation Programme', to provide details of the most urgent priorities over the next 5 years regarding an increase in the UK's climate resilience [46]. Promoting climate action towards the business and civil society sectors is of great significance and is also underlined by the 'Clean Growth Strategy'.

As renewable technology develops and infrastructure deployment increases, it will eventually lead to reductions of GHGs in the energy sector. However, current technologies are not enough to meet energy demands alone, therefore advancing research and development of technologies with multiple applications will help bridge the gap.

The transport sector needs radical transformation. The UK Department for Transport introduced the 'Renewable Transport Fuel Obligation' (RTFO) in 2007, which is the foundation of their environmental policies for combatting climate change [52]. It was released to oversee biofuel regulations within the UK as part of the 'Renewable Energy Directive' [53]. The RTFO has been providing guidance for over a decade to fuel suppliers, and independent verifiers and suppliers of biofuels (external to those under the 'Motor Fuel

Greenhouse Gas Emissions Reporting Regulations' [54]). Part of the RTFO guidance involves assessing biomass feedstocks (including wastes and residues) that are available for biofuel suppliers to apply for 'Renewable Transport Fuels Certificates' (RTFCs), which they need in order to be able to sell biofuels [55]. Biofuels made with wastes and residues may double count under the RTFO, as they are providing resources from wastes that would not otherwise be utilised [55]. RTFCs can be sold on to other suppliers if need be.

The UK government had also pledged actions towards lower emission vehicles before 2015 (<120 g CO_2/km) such as electric, plug-in hybrid, and hydrogen powered vehicles; reducing emissions from shipping and freight, such as ship/cargo fuels (bunker fuel) [56] and aviation fuels (kerosene); and supporting the utilisation of biofuels, including sustainable production and agriculture without impacting food supply [57]. These were covered under the '2010 to 2015 government policy transport emissions' [57], however this policy was withdrawn on the 29th March 2018.

The food vs energy debate could not be explored in full as part of this thesis, due to the multifaceted scale of international variations and market fluctuations, but its influence will be acknowledged.

1.2. Research Goals, Aims, and Objectives

The overriding goal of this research is to assess and understand the environmental sustainability of producing gaseous fuels from biomass for fuel cell applications, with comparisons to competing technologies and fuels.

Biomass benefits from carbon neutrality, through the capture and storage of carbon dioxide (CCS) from the atmosphere within the biomass as it grows [58], as opposed to using fossil fuel sources like coal and gas for providing gaseous fuels; such as hydrogen and methane.

Captured carbon dioxide from industrial processes (like coal combustion plants, gas power plants, and oil recovery [59, 60]) can either be reused within industry processes [61], or stored (CCS) – typically underground (geological storage [59, 62]). It also has potential bioresource and agricultural uses, such as algae (injected into water [63]) and growing crops in greenhouses [61, 64, 65]. Assessment methods for these processes typically involve carbon footprinting, energy balances, and environmental impact assessment [65], the latter is more commonly known as Life Cycle Analysis (LCA).

In this work, the environmental assessment of various biomass conversion techniques was conducted using the internationally recognised LCA method (*Chapter 3*), as per guidance of ISO 14040 and 14044 (*Section 1.3)*. An LCA Software package called SimaPro was utilised to conduct this assessment to produce more accurate case studies and comparisons.

To fully ascertain this environmental assessment technique, several aims and objectives had to be met (*Table 1.1*).

Table 1.1: Thesis Research Aims and Objectives

Reference	Aims and Objectives
A.1.	Explore and understand Life Cycle Analysis (LCA) methodologies and techniques.
A.1-O.A.	Assess an exemplary biomass-to-biofuel system (palm oil biodiesel) by developing a generically-representative Life Cycle Inventory data set.
A.1-O.B.	Analyse the sensitivity of results to life cycle data input and methodological assumptions by comparing respective systems analysis from literature, especially with respect to data variations.
A.2.	Examine the potential of biomass as a future fuel source for fuel cells.
A.2-O.A.	Investigate current biomass pathways.
A.2-O.B.	Synthesise primary data using theoretical methods and match fuels from biomass pathways with the most suitable fuel cell technology(s).
A.2-O.C.	Compare fuels and their associated fuel cell technologies against fossil reference cases.
A.3.	Conduct an LCA comparison of viable biomass pathways.
A.3-O.A.	Select a set of fuel gas production pathways from results of comparison analysis.
A.3-O.B.	Produce a comparative LCA research study of fuel gas production from biomass, and conversion to electricity in fuel cells by utilising literature data, LCA databases within SimaPro LCA software, and the primary synthesised data; including a substance contribution analysis to identify the prevailing burdens driving the pathways impact potential.
A.3-O.C.	Compare the environmental impact of viable pathways with that of fossil fuel reference cases and renewable energy technologies.

A = Aim (1-3). O = Objective (A-C).

There are questions about variations, limitations, and inconsistencies with published studies that need answering. For instance, in some cases different studies analysing the 'same topic' can have dissimilar results; *Chapter 3* will investigate this. The data collection methods used, and completeness of the data sets, are thought to be the main reason for this. An up-to-date comprehensive study assessing specific biomass production methods is yet to be undertaken, let alone utilising the chemical and molecular composition of raw biomass, converted biomass, and the resulting gases, which are explored in *Chapter 4*. There have been singular in-depth studies for specific feedstocks, such as rapeseed oil, one of which was a very detailed UK study [66]. However, using inconsistent units within these studies turn them incomparable, without extensive normalisation, resulting in a lack of

reliability of data. This topic will be explored in *Chapter 3*, using a palm oil case study to demonstrate the extent of variations in published research.

1.3. Thesis Overview

This thesis bridges a research gap across multiple interdisciplinary subjects: environmental and climate science, environmental engineering, chemical engineering, and environmental management. It explores outside of typical chemical engineering boundaries and approaches a relevant topic from the perspective of a climate and environmental scientist, whilst using methodologies from both environmental engineering and environmental management.

This introductory chapter has presented a background of threats of the changing environment, the international governing commitment to reduce GHG emissions, the need for alternative fuels, and how this thesis hopes to approach some of the issues raised, with a focus on biological sources.

Chapter 2 comprises of a literature review, which begins with an introduction to how biomass is being utilised across the energy, heat, and transport sectors. An exploration of the three generations of biomass is then presented, as the different types of biomass sources are discussed, before closing with a review of current literature regarding modern developments in biomass-to-hydrogen conversion techniques.

Chapter 3 will discuss the methodology of LCA and its key concepts, including: goal and scope, the importance of setting system boundaries, inventory analysis (LCI), impact assessment categories and emission indicators, and the interpretation of results to locate hotspots for improvement. A variety of methods that can be used to utilise this assessment resource are also explored, as well as the influence it holds outside of academic research.

In addition, a case study containing data synthesised by normalising secondary data, from which an exemplary study was produced, is included in *Chapter 3*. This case study also investigates the variations in LCI data collection methodologies and conducts a sensitivity analysis of the utilised literature system data. This research has been written as an academic review paper, which was published in October 2018 [67].

Chapter 4 is a systematic analysis of biomass, revisiting from the modern biomass techniques explored in *Chapter 2*. It presents an overview of the current methods of biomass conversion, to extract biofuels and biologically produced gases, and their uses in fuel cells. Thorough evaluations of pathways were undertaken, including calculations of total chain efficiency, fuel gas demand, and raw feedstock demands to identify appropriate methods for fuel gas production and use. Each pathway was compared against fossil fuel derived reference cases. This research has also been submitted as an academic original research paper, which was published in December 2018 [68].

Chapter 5 investigates the processes explored in *Chapter 4*, producing comparative LCA systems, using both characterised and normalised approaches, within SimaPro LCA software. In addition, LCA studies were produced for reference cases: natural gas, fossil hydrogen, the production and maintenance of both 1 MWh electrical SOFC and PEFC systems, and renewable energy technologies (solar and wind equating to 1 MWh output). Sub-system and driving substance contribution impact allocations were explored to demonstrate the sources of contributions to impacts. An academic original research paper has been produced from this chapter's research, which has been submitted for review.

Finally, *Chapter 6* discusses concluding thoughts on the research conducted in this thesis, and further research opportunities that could progress this research field.

CHAPTER 2

CHAPTER 2. REVIEW OF BIOMASS DERIVED PRODUCTS AND THEIR FUEL CELL APPLICATIONS

The purpose of this thesis was to assess and compare biomass derived gaseous fuels for supplying electrical energy from fuel cells, with comparisons of fuel cells running on fossil fuel reference cases, using LCA and ensuring sound methodological choices for data collection (*Chapter 5*). However, to do so, a thorough knowledge of the research fields involved and how this research leads to reliable LCA analysis (*Chapter 3*) is required.

2.1. Availability of Literature

As the world endeavours to reduce greenhouse gas (GHG) emissions and adapt to the impending threat of climate change, whilst achieving sustainable development, cleaner resources are an increasing necessity [69]. However, with the presence of fossil fuels still dominating the energy market, the true extent of how competitive green fuels are compared to fossil resources and current renewable technologies is an on-going question.

This research gap has become clearer throughout this investigation, as the availability of literature depends on the level of activity in the research field, which subsequently determines the number of publications and the more prevailing topics. Therefore, in order to find relevant sub-topics within larger areas of research, more precise searches are required (as seen in *Table 2.1*). The initial search was conducted in August 2018 on Science Direct to locate publications with the specific key words to identify the total number of publications for each research field between 2008 and 2018. Other publication search engines were also used (Google Scholar and Scopus) but they did not return as many results. Therefore, Science Direct was assumed to have the greatest level of accuracy for finding 10 years of research publications.

Table 2.1: Literature coverage across biomass related fields in the last decade (2008-2018) on ScienceDirect, including the percentage contribution of more precise fields.

Research Fields	Overarching fields		Sub-research fields	
	No. of publications	*% of field*	*No. of publications*	*% of field*
Biomass	203,834	100%		
First Generation Biomass			*65,090*	*31%*
Second Generation Biomass			*53,059*	*26%*
Third Generation Biomass			*32,057*	*16%*
Waste Biomass	71,872	100%		
Biofuels	42,618	100%		
Biofuels from Waste Biomass			*16,881*	*15%*
Biodiesel	25,455	100%		
Biodiesel fromWaste Biomass			*9,114*	*36%*
Gaseous Biofuels	7,989	100%		
Gaseous Biofuels for Fuel Cells			*3,681*	*46%*

2.2. From Mass to Gas

The term 'biofuel' typically is used to represent liquid fuels for transport made from biomass, but should also be extended to gaseous fuels [70]. There are three generations of biomass, the second and third attempting to provide alternative fuel sources outside of current food markets.

2.2.1. First Generation Biomass

First generation biomass is made up of agricultural crops and is typically based on oil or starch, such as in sugar cane, maize, wheat, rapeseed, and palm fruit [71-74]. These feedstocks can each be passed through different processes to make different products. For instance, wheat and sugar cane are used to produce ethanol by fermentation [74, 75]. However, their use comes with a price. For the most part these crops are also traded in food markets, so if stock is taken from the food system into the energy system, there are

concerns that the food market will be affected due to the potential conflict between food and energy pricing, and products to the energy markets [71, 75, 76].

Current applications of first generation biomass produce a variety of substances [77, 78] through processes such as: pyrolysis and liquefaction (dry and wet biomass to bio-oil and syngas), metabolic processing (algae photosynthesising hydrogen), and anaerobic digestion and fermentation (bacteria producing biogas and biomethane, and methanol and ethanol) [79-81] via transesterification. Oil rich biomass, like rapeseed and palm, are steamed and pressed for oil extraction, which is used to produce crude oil, and refined to biodiesel [82-84]. This process involves mixing the crude oil with ethanol or methanol and a catalyst of sodium hydroxide [85, 86]. This converts triglyceride oils into methyl esters, which are then washed to remove the glycerol, thus producing biodiesel [69, 84].

Separating the glycerol from the biodiesel allows the biodiesel to burn up to 75% cleaner than conventional diesel, when used in an unmodified diesel engine [87]. This process can be run at different temperatures dependant on the desired reaction rate and yield of esters. Published research shows promising results for increased temperatures, and that active catalysts increase the efficiency of ester conversions [88-90]. It has also been found that blending with biodiesel reduces exhaust emissions in the transport sector [91, 92] and has a higher biodegradability, amongst other advantages beyond the agriculture, transport, and energy sectors with by-products and wastes providing substitute products and feedstocks for gas production (fermentation, anaerobic digestion, *etc*).

Biodiesel has a comparable performance to conventional diesel, with benefits of carbon dioxide emissions from biological sources resulting in neutral emissions due to short term temporal removal from the carbon cycle. As opposed to fossil diesel, which has had long term temporal removal, therefore resulting in net carbon emissions. It has several

advantages in terms of political support around the world, including in the United States and Europe, in reducing the dependency on imported conventional diesel. The production of biodiesel increased internationally from 2.4 billion litres $^{yr-1}$ in 2004 [93] to 120 billion litres^{yr-1} in 2017. There are also expectations of further increases up to 131 billion litres $^{yr-1}$ in 2027 [94]. Similarly, ethanol production was seen to increase from 28.5 billion litres $^{yr-1}$ in 2004 [93] to 36 billion litres $^{yr-1}$ in 2017, with expectations of up to 39 billion litres in 2027 [94]. In comparison to the 290 billion litres $^{yr-1}$ (256.7 million tonnes) of diesel that was produced internationally in 2016 [95], giving biodiesel a potential market share in the order of magnitude of 50% of the diesel market.

The economic benefits of biodiesel include by-products with added value, job creation, and investment into plants and equipment [96]. The need for transport fuels will continue to grow as more vehicles join the world's roads and pressure rises on governmental commitments to reduce emissions [97-99]. With the transport industry also causing some of the highest percentage of greenhouse gas emissions, the need to produce a greener fuel without compromising land is a growing priority [100].

However, there are issues of land use and resource allocation across Europe, in terms of what can be grown where and contribute to the production of biofuels, and further issues of sustainability and renewable sources on a global scale [101]. The most predominant issues are the reallocation of cultivated agricultural land and deforestation to provide space to grow the desired feedstock varieties. The act of deforestation increases biogenic carbon release, and the use of cultivated land for energy crops can increase Eutrophication Potential and Acidification Potential impacts, due to increased fertiliser use [102].

The purpose of biofuels is to reduce the GHG emissions from the transport industry, but if growing the feedstock and turning it into said biofuel is more energy and carbon intensive

than what it is trying to substitute, then the true extent of its sustainability must be identified. A way to reduce this impact is to only use the agricultural waste residues that are either not used as food or have a different market to food. This is where second generation biomass advances.

2.2.2. Second Generation Biomass

Lignocellulosic agricultural wastes (corn stover/cereal straws), purpose grown grasses (jatropha/miscanthus/switch grass), forestry waste residues, and organic municipal wastes are the main feedstock examples for second generation biomass [69, 71, 74]. They can be utilised in gasification (for syngas), pyrolysis (for bio-oil), and anaerobic digestion (for biogas and biomethane), which have their specific markets within the energy and transport sectors.

The benefits of second generation feedstocks are that they have lower GHG emissions, do not interfere with existing markets, and decrease land competition [74, 103]. In addition, for wastes, most of their production impacts are associated with their primary produce. Waste products can be 'burden free' (within reason). This means that any environmental impact from the production of the primary product, from which a useable waste can be sourced from its waste stream, the impact burdens are allocated to the primary product instead; the useful waste is therefore free of all burdens its previous production system has [104, 105].

For example, a product made from useful waste(s) would only carry the impacts of its processing, manufacture, and use. This is because the useful waste is replacing another product that would have had to be made from scratch, therefore causing avoided burdens [106] *i.e.* using palm kernel oil cake waste by-product for animal feed, rather than disposing of it, will have a far lower environmental impact than the life cycle of growing and producing

animal feed, which also, by the way, reduces the price of the animal feed without compromising on nutrition [107, 108]. This is known as 'burden crediting' and is important for reducing the environmental impact of products that have viable substitutes from waste streams.

Utilisation of forestry waste residues, as opposed to first generation energy crop feedstocks, has no impact on the food market. This is because subsidies for biomass cultivation on agricultural land have shown an increase in food prices, as farmers may receive more money producing biomass for energy conversion than for food production [109-111]. Therefore, if the biomass is sourced outside of the agricultural market, there will be less pressure on arable land.

However, it must be made clear that wood designated for timber yards or logging is not classified as second generation biomass, as that would interfere with an existing market. Only recovered consumer wood, wastes/residues from the logging industry (sawdust, bark, and wood shavings, also known as 'hog fuel' [112]), and mill rejects are to be considered [113, 114]. For instance, up to 60% of the total harvested trees and resulting residues are often unused and would otherwise be combusted or left to decompose [115, 116]. The most prominent alternative use of forestry residues is pyrolysis for bio-oil production, which can be refined into diesel, petroleum/gasoline, and kerosene (*Section 2.4.1*).

2.2.3. Third Generation Biomass

This uses macro and microalgae, such as seaweeds and green/blue-green algae, as an oil rich feedstock and processes utilising completely new bio-synthesis [74]. Algae are a naturally rich source of lipids, which varies between species in terms of dry weight percentage – up to 80% [109]. This makes them more efficient as raw material than first generation feedstocks [117]. Green algae have been extensively studied and found to be

one of the best microalgae feedstocks, as within the dry biomass they can comprise of up to 51% lipid content [118].

However, there are mass inconsistencies between algal studies, in which: their inventories have limited or no comparable parameters; different reactor technologies are utilised, which would produce incomparable yields; and the scale of each system are not scalable against the others. These factors affect the reliability of any review studies combining these assessments, especially regarding the diverse growth methods for different applications for algae (i.e. increasing algal mass growth for biodiesel or maintained growth for hydrogen production). Also, the sheer amount of space required for growing algae involves extensive amounts of investment and energy to nurture the algae to a harvestable state. For instance, in order to generate 1 kg of Biodiesel, microalgae need 3,726 kg of water, 0.44 kg of nitrogen and 0.71 kg of phosphate if the water used is fresh and not recycled [119]. On the other hand, microalgae grown in sea water decrease the water requirement by 90%, and just require this 0.71 kg of phosphate for nutrition [119].

Alternatively, green and blue-green algae can be utilised for hydrogen production via metabolic processing, using photobiological processes. They can be cultivated within photobioreactors, which are irradiated by natural or artificial light to produce yields of 1 tonne H_2/day, 360 tonnes/year, over a 100 km^2 area. Annually this requires 115,000 kg of water and 25,000 tonnes of carbon dioxide. Research is ongoing regarding the possibilities of using the bioreactors to treat agricultural wastewater, which fulfils the algae's water, carbon dioxide, and nutrient demands [120-122]. However, the primary research objectives for algal biomass growth are for liquid fuel production via hydrothermal liquefaction [123, 124], not hydrogen production.

Studies on these different generations, and how best to utilise them, are continuing. However, the second and third generations require further research, ground-breaking developments, investment, and industrial action to develop towards the production of sustainable biofuels.

2.3. The Biomass Revolution

Biomass is currently being used for supplying heat and electricity to the domestic and industry sectors, with the majority coming from solid biomass [125-127]. The growing acceptance of biomass within the energy industry has resulted in several additional methods of utilisation, mostly by converting it into fuel gases. Some of these conversion processes are today competitive against current fossil methods [128]. The dominance of second generation biomass is growing in this field, as technology moves away from first generation biomass, whilst also exploring third generation biomass. Gasification, fermentation, and anaerobic digestion are the largest research areas within the biomass field (*Table 2.2*), as they can utilise all three generations of biomass.

This literature search was conducted in August 2018 on Science Direct using specific key words to identify how many papers each research field and pathway has had published between 2008 and 2018. Like *Table 2.1*, other publication search engines were also used (Google Scholar and Scopus) but they did not return as many results.

Table 2.2: Estimated literature coverage across biological and thermochemical conversion fields and pathways in the last decade (2008-2018) on ScienceDirect, including the percentage contribution of biomass related pathways.

Research Fields and Pathways	Unfiltered		'Biomass'	
	No. of publications	*% of field*	*No. of publications*	*% of pathway*
Biological Conversion	**163,107**			
Anaerobic Digestion	*48,074*	*30%*	*22,245*	*46%*
Metabolic Processing	*30,353*	*18%*	*1,119**	*4%*
Dark Fermentation	*29,451*	*18%*	*8,991*	*31%*
Light Fermentation	*55,229*	*34%*	*16,091*	*29%*
Thermochemical Conversion	**165,618**			
Gaseous products	***79,587***	***48%***		
Gasification	*73,027*	*92%*	*33,460*	*46%*
Supercritical Water Gasification	*6,560*	*8%*	*4,042*	*62%*
Liquid fuel products	***86,031***	***52%***		
Pyrolysis	*68,782*	*80%*	*21,255*	*31%*
Liquefaction	*17,249*	*20%*	*4,895*	*28%*

** Filtered with "Algae" instead of "Biomass".*

Between 2008 and 2018, the estimated total of 'biological conversion' pathways published was 163,107; 'dark fermentation' and 'light fermentation' pathways jointly being the most published, followed by 'anaerobic digestion'. Of all searched anaerobic digestion publications, less than half were directly related to 'biomass', whereas only 4% of research papers covered 'metabolic processing' from 'algae'. The majority of fermentation studies were found to focus predominately on ethanol production, and 31% to 29% utilised biomass opposed to municipal wastes.

165,618 research papers on 'thermochemical conversion' pathways were also published in the last 10 years; consisting of pathways producing gaseous products (79,597 papers, at 48% of the overarching field) and 86,031 papers producing liquid fuel products (52%). Nearly 75,000 'gasification' studies, with less than half using biomass (with the rest using coal), were published. However, 'Supercritical Water Gasification' ('SCWG') was the least

covered research field, with only 6,500 papers published; although, unlike gasification, over 60% were related to 'biomass'. Regarding liquid fuels, 'pyrolysis' papers totalled at 80%, with 31% consisting of fuels from biomass, and 'liquefaction' papers made up the remaining 20%, with 28% of these papers utilising biomass.

How these pathways interact with each other, share clean-up processes, and feed specific markets (heat and electricity, liquid fuels, and gas grid) is detailed in *Figure 2.1*, with Section numbers referencing specific pathways explored in this chapter. They can also utilise a variety of biowastes to make gaseous fuels, particularly hydrogen, methane, and syngas. In addition, gases not directly usable within certain fuel cell technologies can be upgraded through water-gas shift reforming or steam methane reformation. These are the two most prominent technologies for obtaining hydrogen, if it is not produced directly.

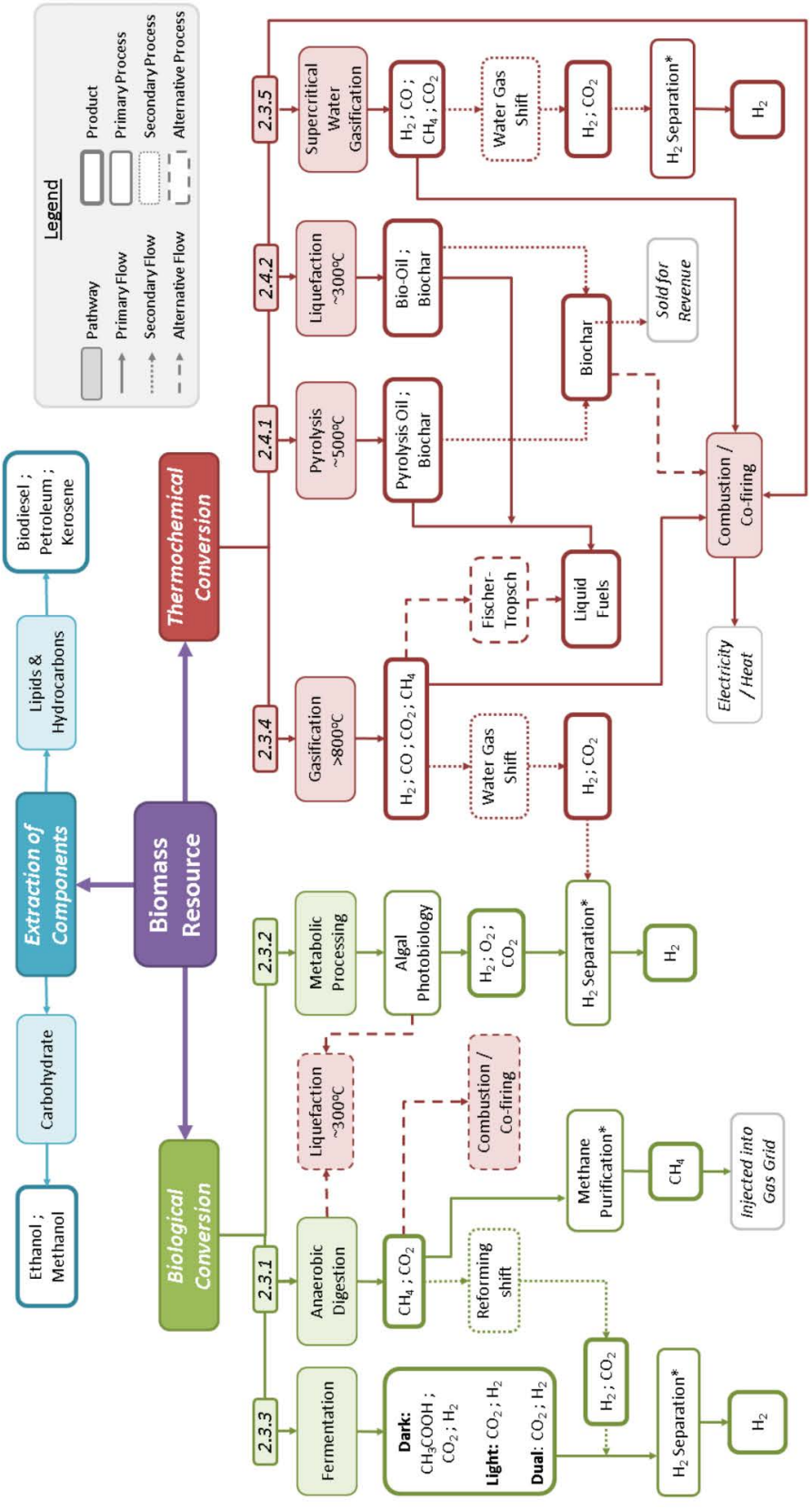

Figure 2.1: Biomass to gas conversion pathway tree, with labelled pathways for corresponding Chapter 2 Sections

Adapted from: [129, 130]

* A '*Hydrogen Separation*' and '*Methane Purification*' stages are where gas mixture components are removed to produce pure hydrogen and methane, typically via pressure swing adsorption (PSA).

***NB**: 'Reforming Shift'* refers to steam methane reforming (*Section 2.6)*

2.3.1. Anaerobic Digestion

There are many types of anaerobic digesters, the most popular being tanks and lagoons (*Figure 2.2*). Vertical or horizontal insulated tanks are the most dominant type of digester, allowing for gravitational separation, and 'batch flow' processes with typical batch lengths of 15 to 20 days [131, 132]. Alternatively, there are 'continuous flow' digester tanks where new feedstock is added continuously. Vertical tanks are typically found in industrial and agricultural applications, as they have been found to be easier to maintain, but also cheaper to build [132, 133].

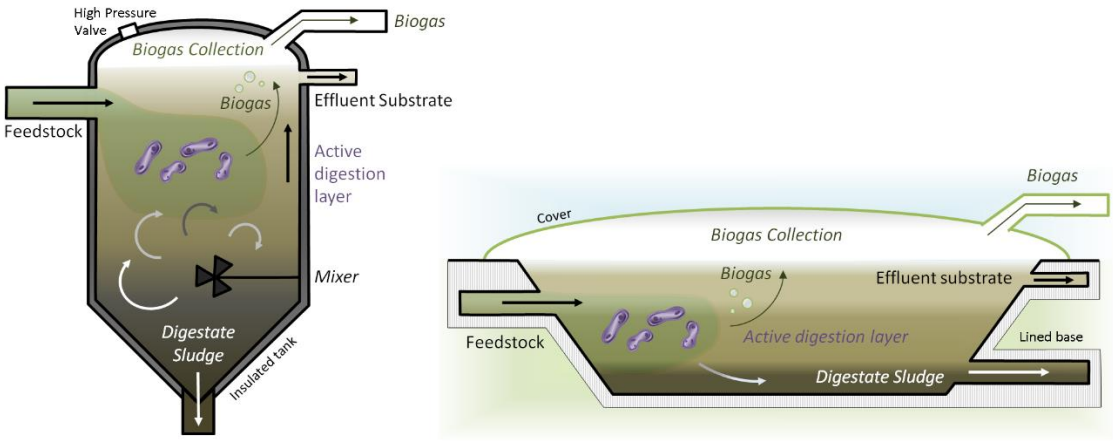

Figure 2.2: Anaerobic digester reactors: Vertical tank reactor (left). Sealed and lined lagoon (right).
Modified from: [134-136]

On the other hand, 'horizontal plug flow' lagoons are predominately utilised in warmer climates on agricultural plantations or farms [137, 138]. When used in naturally warm climates, the lagoon digester does not need to be heated, and so maintains the bacteria culture naturally. Both reactors can either be singular, as shown, or be multiple digesters, meaning they have primary and secondary stages for digestate separation, a higher yield, and better process control [132]. The majority of rural and less developed farms with open wastewater treatment lagoons would be able to upgrade their infrastructure with the help of government subsidies [139, 140] and capture gases for their onsite energy use or sell it to the grid [138, 139].

Inside the reactor, four reactions take place: Hydrolysis, Acidogenesis, Acetogenesis, and Methanogenesis [141] (*Figure 2.3*).

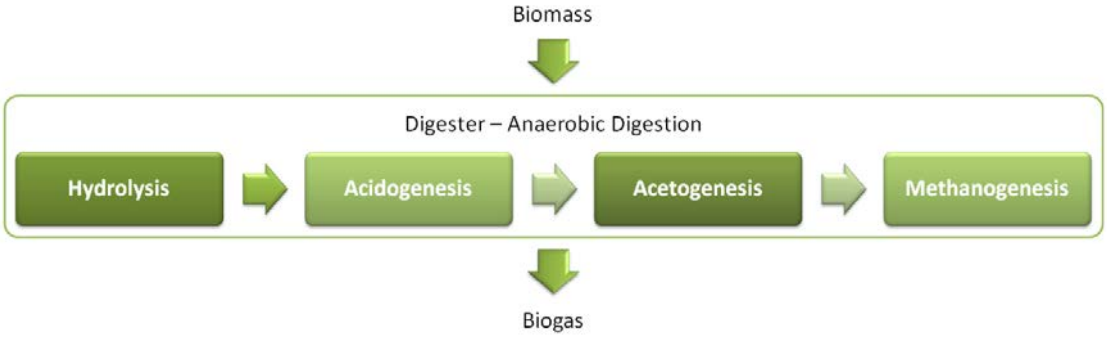

Figure 2.3: The fundamental steps of anaerobic digestion
Modified from: [142]

Firstly, bacteria break down the wet biomass, e.g. polysaccharides such as starch or cellulose ($C_6H_{10}O_4$) into monomers, dimers, and smaller oligomers (glucose $C_6H_{12}O_6$, sucrose, and fructose), and into hydrogen, via hydrolysis (*Equation 2.1*) [143]. Potential biomass that can be used are animal slurry, sewage water and sludge, energy crops, and biomass residues from agriculture and food processing [144, 145] or bioreactor sludge/wastes (*Section 2.2.2*).

$$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + H_2 \qquad [2.1]$$

In the second stage, acidogenic bacteria use the carbohydrates to produce alcohols (CH_3CH_2OH), carbon dioxide, propionic acid (CH_3CH_2COOH), and water (*Equations 2.2 to 2.3*) [143]. Further reactions take place during the third stage, in which acetogenic bacteria produce acetic acid (CH_3COOH), carbon dioxide, and hydrogen (Equation 2.4) [143, 146].

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2 \qquad [2.2]$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O \qquad [2.3]$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \qquad [2.4]$$

These three stages are essentially what occurs during biomass dark fermentation (*Section 2.3.3*). Anaerobic digestion has a fourth stage, methanogenesis. This is where methane

forming bacteria (mesophilic for cultures at ~35°C or thermophilic at ~55°C [131, 132, 147]) convert carbon dioxide, hydrogen, and acetic acid into water and biogas (*Equations 2.5 to 2.6*) [143, 146]. The overall reaction for this pathway is represented in *Equation 2.7* [146, 148].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad [2.5]$$

$$CH_3COOH \rightarrow CH_4 + CO_2 \quad [2.6]$$

$$C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4 \quad [2.7]$$

Thermophilic bacteria produce greater amounts of biogas per kg of feedstock, which allows them to be used in smaller capacity tanks, as well as effectively removing pathogenic organisms due to the higher temperatures [131, 132]. On the other hand, mesophilic bacteria use less energy intensive systems, which make them a cheaper (and therefore more prevalent) option [132].

Biogas can be captured in a sealed digester and utilised the same way as natural gas (directly in boilers [140, 149-151]). By removing contaminants and the carbon dioxide content, it can be upgraded to biomethane (pure methane of biological origin), which can be used in more specialised power generating units, such as gas turbines and fuel cells [144, 152, 153]. This is typically completed by Pressure Swing Adsorption (PSA), which is a gas separation technique in which a gas stream is fed across a permeable membrane, with a liquid solvent on the other side. Each side has fluctuating pressures, which drives the separation process. Unwanted gases are absorbed into the membrane while under high pressure conditions [154], and are desorbed into the solvent on the opposite side via low pressure conditions [155]. This process is typically used to separate methane from carbon dioxide in biogas, and hydrogen from oxygen, syngas, or even natural gas [156, 157], but various other gas specific membrane technologies are also available [158-160]. Example technologies include: vacuum pump powered nanometre hydrogen separation membranes

within the bioreactor [161], synthetic membranes [162], and rare metal membrane reactors [163].

Undigested feedstock leaves the digester as digestate sludge, which can be utilised in fermentation (*Section 2.3.3*), for further digestion, or as a fertiliser substitute to return minerals and other nutrients to the land.

2.3.2. Metabolic Processing

There are two types of metabolic processing, direct and indirect biophotolysis, based on different species of algae. For technically meaningful hydrogen production, the algae are cultured in photobioreactors, which have four common designs: raceway pond, flat plate, tubular and vertical-column (*Figure 2.4)*. These bioreactors vary between being used for algal biomass production, and/or gaseous products. Whilst raceway ponds are the most utilised system for hydrogen production, flat plate bioreactors yield higher rates of algal biomass, for instance for biodiesel production [164, 165].

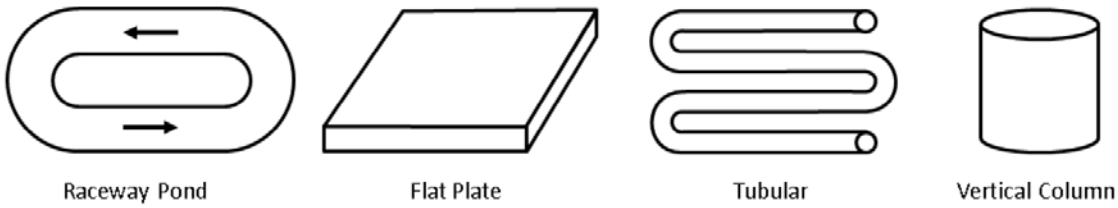

Figure 2.4: Different Photobioreactor Designs for Microalgae Cultivation.
Modified from: [166-169]

The land requirements for each type of bioreactor is determined by the desired product; algal biomass or gases. For instance, the National Renewable Energy Laboratory (NREL) in the USA have proposed a pilot plant over 100 km^2 to produce 360 tonnes of hydrogen gas each year (*Figure 2.5*).

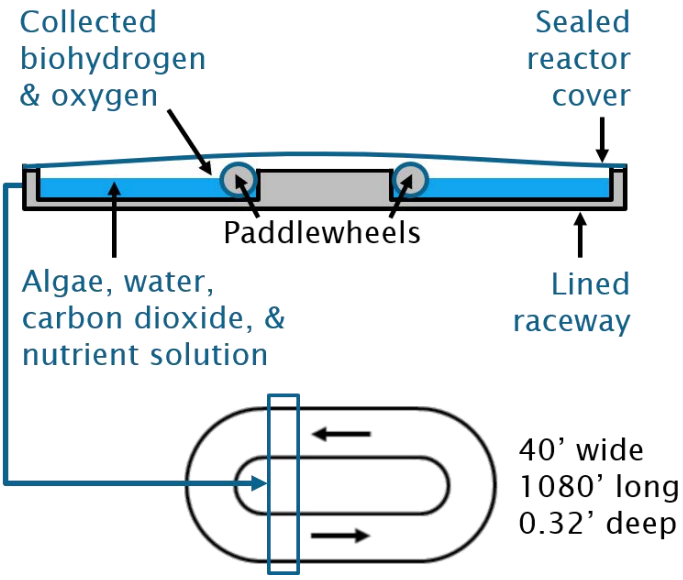

Figure 2.5: Algal Raceway Photobioreactor Design.

Modified from: [63, 170]

This site would contain 20 sealed raceway photobioreactors, and cost around $2 million to construct [63, 170]. It is imperative that gas production systems are sealed to capture all yields. Open systems are only suitable for biomass growth.

i. Direct Biophotolysis

Direct biophotolysis typically uses green microalgae, such as *Chlamydomonas reinhardtii,* for undertaking photosynthesis and splitting water using light as energy source [171, 172] (*Equation 2.8*) [81, 173]. *C. reinhardtii* have the potential to undertake solar energy conversion up to ten times more effectively than trees [174]. This is due to the presence of hydrogenase enzymes, which convert the separated protons (H^+) into molecular hydrogen [171] *(Figure 2.5)*.

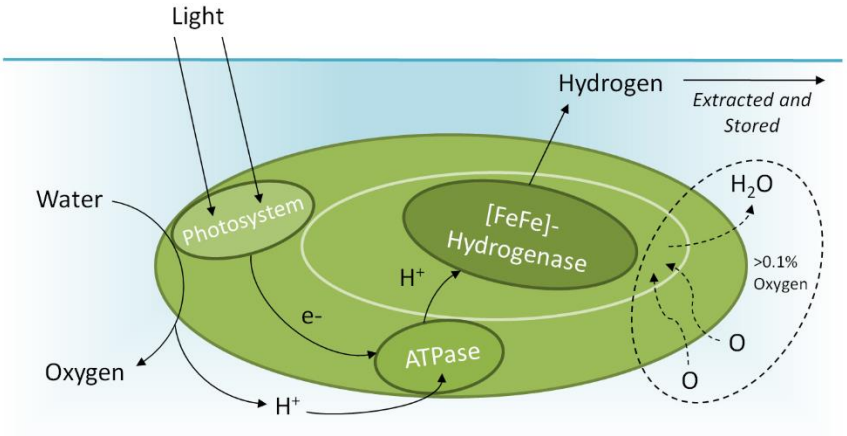

Figure 2.6: Direct biophotolysis of hydrogen

Simplified from: [166]

[FeFe]-hydrogenase has higher enzyme activity compared with [NiFe]-hydrogenase [166, 175]. However, it requires energy (e- electron carrier) inputs, which slows the rate of biohydrogen production as they have to be obtained from light photons (*Equation 2.9*) [176].

$$Photons + 2H_2O \rightarrow 2H_2 + O_2 \qquad [2.8]$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad [2.9]$$

In addition, if oxygen production exceeds 0.1%, the hydrogenase enzyme is inactivated [177], thus inhibiting biohydrogen production as hydrogen oxidises with oxygen back into water [166, 178]. Research regarding the effect of oxygen on hydrogen yields have developed algal mutations and enzyme manipulation, to decrease the oxygen inhibition [179-181].

ii. Indirect Biophotolysis

Indirect biophotolysis is when blue-green microalgae (cyanobacteria), such as *Anabaena variabilis,* are grown under normal cultivated conditions, using light to fix carbon dioxide into carbohydrates, and split water [171, 182, 183] (*Equations 2.10, 2.11, and 2.12*) [81, 173]. The carbon dioxide has to be injected and dissolved into the water within the bioreactor in order for this reaction to take place efficiently [166]. The carbohydrates

produced by the microalgae are used as a substrate by nitrogenase to produce hydrogen during the ATP phase (*Equation 2.13*) [173, 176]. The photons deliver the energy for dissociation (6x 285 kJ/mol $_{H2O}$).

$$Photons + 6H_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2 \quad [2.10]$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2 \quad [2.11]$$

$$Photons + 2CH_3COOH + 4H_2O \rightarrow 8H_2 + 4CO_2 \quad [2.12]$$

$$2H^+ + 2e^- + 4ATP \rightarrow H_2 + 4ADP + 4Pi\ (inorganic\ phosphate) \quad [2.13]$$

Unlike direct biophotolysis, this process has no inhibition from oxygen concentration due to nitrogenase in particular strains of cyanobacteria [181, 184] used in this process having thicker cell walls [166], which slows the diffusion of oxygen (*Figure 2.6*).

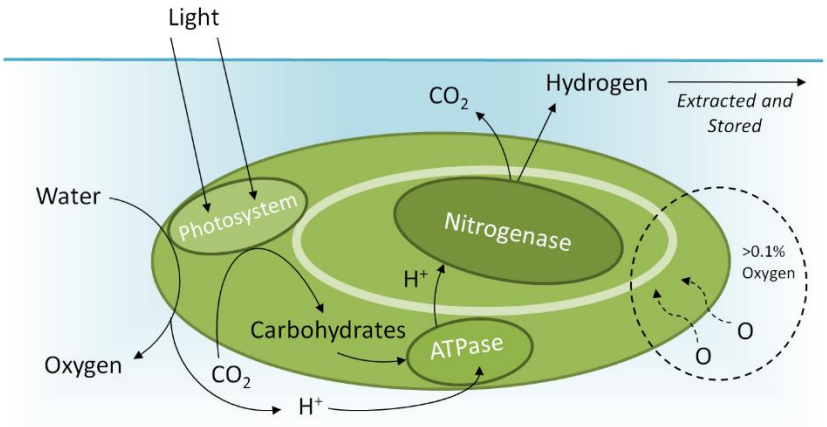

Figure 2.7: Indirect biophotolysis of hydrogen
Simplified from: [166]

iii. Metabolic Processing Advancements

There has been substantial research into the variations of biohydrogen production per species of microalgae, of which green and blue-green microalgae are currently the most popular as they are well-known for their biohydrogen production abilities. However, they are not the most efficient due to the biological limitations of the organisms driving the reaction. The algae capable of producing hydrogen typically have a maximum production efficiency of 10% [161, 181]. This has led to advancements in the field as researchers conduct genetic modifications to improve performance and promote immunity against

oxygen inhibition [182, 184, 185]. On the other hand, there are few hydrogen-specific studies that offer comprehensive data due to the lack of publications beyond national research laboratory results, like the NREL in the USA [63, 166, 170]. Most algae studies are conducted for biofuel production, such as biodiesel and bioethanol, which use the algae biological matter, not their gaseous products, and are a potential biological source to replace oil based fuels [186-189].

Like anaerobic digesters, the bioreactors produce a by-product of sludge, which is essentially dead algal biomass. This biomass can be utilised for fermentation feedstock, but it is preferred to integrate direct biophotolysis with dark fermentation processes, in order to directly utilise carbohydrates within the waste bioreactor sludge as feedstock [166]. This primarily increases the amount of biohydrogen produced but also allows carbon dioxide recycling. The heterotrophic bacteria used in dark fermentation anaerobic conditions produce carbon dioxide, instead of fixating it [166], alongside acetic acid and biohydrogen. Carbon dioxide is captured and pumped back into the photobioreactor, where microalgae fixate it into carbohydrates.

Therefore, as both indirect and direct biophotolysis produce pure hydrogen, they have potential for all fuel cell technologies. In order to obtain pure hydrogen without oxygen contamination, collected gases need to be separated, either via PSA or by specialised membranes [63]. Potentially, this can be done during the hydrogen generation process and would prevent inhibition taking place [172] (see *(i)*). The pure hydrogen can then be used in fuel cells straight from storage.

2.3.3. Fermentation (Dark & Light)

Fermentation is typically associated with alcohol production from crops, such as maize and wheat. In regard to producing hydrogen from biomass waste residues, fermentation can be

conducted in two separate ways, each within gas tight bioreactors with either dark (no sunlight) or light (well lit) anaerobic conditions [190, 191], similar to that of anaerobic digestion.

Heterotrophic bacteria (which thrive in dark conditions), such as *C. butyricum,* break down carbohydrates and water in organic biomass wastes into acetic acid, carbon dioxide and biohydrogen (*Equation 2.14*) [173]. Anaerobic digestate (and bioreactor) sludges can be added so that any remaining components can be converted for optimum hydrogen yields [192, 193]. Phototrophic bacteria, such as *R. sphaeroides*, use light to break down acetic acid and produce carbon dioxide and biohydrogen (*Equation 2.15*) [173, 193].

Recent developments in fermentation have provided systems such as combined dark and light fermentation, in which cellulose and starch rich feedstocks are pre-treated and fermented into organic acids, carbon dioxide and hydrogen via dark fermentation [177, 194], conducted in dark, anaerobic conditions, where hydrogen production is consistent [195]. Additional hydrogen and carbon dioxide are then produced as conditions swing to that of light fermentation, in anaerobic conditions [196-198] (*Equation 2.16*). Photoheterotrophic bacteria have excellent biomass to hydrogen ratios, with 80% being previously achieved in 2008 [80]. Research was also conducted in 2012, converting glycerol to hydrogen, achieving 96% efficiency [199] The produced mixed gases from both systems then follow the standard procedure of separation and purification via PSA, before being compressed and stored.

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad [2.14]$$

$$Photons + 4H_2O + 2CH_3COOH \rightarrow 4CO_2 + 8H_2 \quad [2.15]$$

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2 \quad [2.16]$$

Some photoheterotrophic bacteria can also be used in dark conditions to perform a reversible biological water-gas shift (bio-shift), which is where carbon monoxide and water are formed into carbon dioxide and biohydrogen [200, 201] (*Equation 2.17*) [81].

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad [2.17]$$

However, typical hydrogen production yields are below 10 to 15% [191] (with respect to the total hydrogen available) due to the biological process limitations. The theoretical production rate for biomass fermentation ranges from 2 $mol_{hydrogen}/mol_{glucose}$ to 4 $mol_{hydrogen}/mol_{glucose}$, depending on the feedstock and the end products, such as acetic acid or butyric acid [171, 202, 203]. The same gas purification methods mentioned in *Section 2.2.3* can be applied to fermentation bioreactors for gas separation and pure hydrogen extraction.

A study by Djomo & Blumberga [198] assessed three biohydrogen pathways that utilised agricultural food wastes to produce hydrogen via the dual process of dark and light fermentation, in which hydrogen yields were produced utilising feedstocks of wheat straw, sweet sorghum stalk, and steam potato peels. All are high in carbohydrates, abundant, and inexpensive as they can be collected from agricultural waste streams (second generation biomass) [198, 204]. Fermentation requires suitable substrates such as carbohydrates, sugars, starch, and cellulose in order to produce hydrogen efficiently, however, feedstock efficiency only goes so far and the production system must be equally, if not more, efficient in order to make the system profitable [204].

Co-products and waste products are the most influencing factors that can be utilised in hydrogen production. For instance, in hydrogen production processes where carbon monoxide is produced, the system combines it with water to utilise a water-gas shift,

reforming it into carbon dioxide and hydrogen. This process is already said to be high intensity concerning electricity use, but there is a biological alternative.

Some photoheterotrophic bacteria, which are used in light fermentation, can survive in the dark by using carbon monoxide for energy, producing hydrogen as a by-product of this process [79, 81, 205]. It has been reported that 1 kg of photoheterotrophic bacteria can produce 1 kg hydrogen per day in systems such as fixed bed reactors [206]. Utilising additional biological methods like this within dark and light fermentation reactors, as well as feeding by-product gases from external processes, such as steam methane reforming, would increase the hydrogen yield without increasing its environmental impact. This process is referred to as 'Bio-Shift' in *Figure 2.1* (also referenced *Chapter 4)*.

2.3.4. Gasification

Conventional methods of gasification traditionally involve feedstocks such as coal, which used to produce syngas for town-gas networks or in the future in high-performance coal fired power plants [207-209]. For the utilisation in biomass conversion, there are three stages: upstream processing, gasification, and downstream processing. Upstream processing consists of sizing the biomass, drying, and preparing the gasifier agents (air, oxygen or steam [210, 211]). Lignocellulosic biomass from forestry wastes (logging, sawmill, tree, and shrub residues [212]), agricultural residues (animal and crop wastes), and energy crops (corn and grasses) are gasified at high temperatures to produce syngas [213], a gas made up predominately of hydrogen and carbon monoxide (*Equation 2.18* - modified from [214-216]). Downstream processing consists of tar removal, gas clean-up with catalysts, and reforming to produce more hydrogen, depending on the end application [216, 217].

$$Heat + 2C_6H_{10}O_5 + 4H_2O \rightarrow 10H_2 + 6CO + 4CO_2 + 2CH_4 \qquad [2.18]$$

Gasification typically operates around 700°C. To achieve tar-free gasification, higher temperatures are required (>1,200°C [213]). Syngas has different compositions depending on whether pure oxygen, steam or compressed air are used as a gasification agent, in which case methane and nitrogen are present with air, but are absent with oxygen [218]. Depending on the gasifier reactor type and the gasifier agent used, the composition of the gases produced changes: fixed, entrained, or fluidised bed gasifiers [219-221] (*Figure 2.7*), as well as rotary kiln and plasma reactors [222]. Fixed beds are the most traditional gasifiers, operating with a uniform air flow, with alternatives being downdraft, updraft, crossdraft, bubbling, or circulating [220, 222, 223]. *Figure 2.7* demonstrates: (a) updraft fixed bed reactor, (b) downdraft entrained bed reactor, and (c) bubbling fluidised bed reactor.

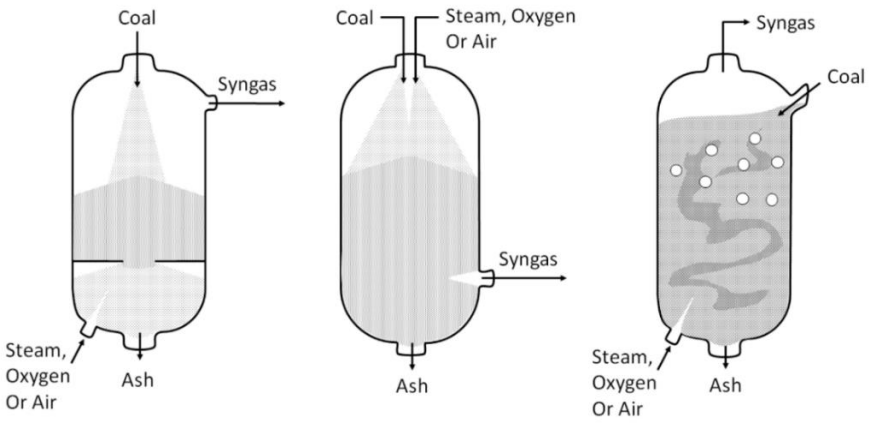

Figure 2.8: Gasifier types: Fixed bed (left), entrained bed (centre), fluidised bed (right).
Modified from: [220, 224]

Fixed bed gasifiers typically have biomass enter from the top and the gasifier agent blown in from below (updraft gasifier) [220, 224]. Syngas is collected towards the top of the gasifier, with ash removal occurring at the base. Fluidised bed gasifiers vary significantly in that biomass is entered as pulverised feedstock and supported by an air bed, thus being better accessible to the gas phase reactants through constant stirring by gas bubbles [220]. Entrained bed gasifiers have both biomass and gasifier agents enter at the top of the gasifier [220, 221], with syngas being extracted from the side. This method produces slag

instead of ash, due to higher temperature levels, which is extracted at the base of the reactor.

Depending on whether the gasifier agent is pure oxygen, air, or steam, the reactants and environment within the gasifier are a key influence on the gas composition [221]. It is possible to produce syngas with higher hydrogen and carbon monoxide content, which results in syngas with a higher heating value but can also affect the efficiency of the process [217, 219, 225]. This is because gasifiers that require dry, hot conditions for optimum efficiency struggle with wet biomass/added humidity as it increases the energy demand by drying prior to reaction [226].

Recent development of gasification technologies has resulted in Integrated Gasification Combined Cycle (IGCC) power plants [207-209], which had two turbines that utilise the syngas within the power plant as a fuel blend, and another that uses the steam by-product from this high temperature process. This technology can also be integrated with fuel cells and carbon capture and storage [208, 227, 228]. Coal is predominately used as the initial fuel, but with the increasing addition of lignocellulosic biomass, any bio-carbon dioxide within the captured flue gases will be carbon negative, as the sequestrated carbon during the biomass' growth will not be released back into the atmosphere (which would make it carbon neutral).

Within literature, Moreno & Dufour [223] conducted research in Spain on gasification of forestry wastes. They assessed pine, eucalyptus and pruning waste from grapevines and almonds, in a fixed bed gasifier. The study used a Functional Unit (FU) of 1 Nm^3 of hydrogen (normal cubic meter) with 99.9% purity, which would be obtained from refined syngas using PSA. This is where syngas is separated as different gases are removed by passing the gas across the membrane at different pressures and are transmitted into a solvent on the

other side. An additional stage of water-gas shift reaction was also included in the assessment, in order to increase the hydrogen yield [223].

2.3.5. Supercritical Water Gasification

It is from experimentations in gasifier conditions that SCWG eventually evolved, which was first researched in the 1970s [226]. Here, wet, high lignin biomass (wood) is gasified at high pressure (>22.1 Mpa) and high temperature (>374°C) conditions [229], which turns the moisture in the biomass supercritical (*Figure 2.8*). The lignin breaks down into cellulose and hemicellulose, dissolves into carbohydrates [230], and then reforms into syngas [230, 231].

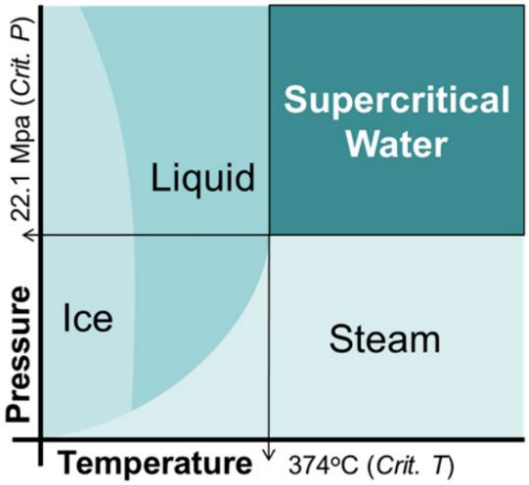

Figure 2.9: Supercritical water conditions.
Modified from: [229]

Hydrogen concentrations within the syngas are higher when temperatures exceed 600°C, whereas at temperatures under 450°C more methane is produced [232]. The higher moisture conditions produce syngas with lower hydrocarbons and higher carbon monoxide and hydrogen contents, compared to conventional gasification [231, 232] (*Equation 2.19) (Modified from* [233]).

$$Heat + 2C_6H_{10}O_5 + 5H_2O \rightarrow 13H_2 + 7CO + 4CO_2 + CH_4 \qquad [2.19]$$

SCWG can handle any material that contains hydrocarbons, including hazardous materials, and break them down into the basic constituents in analogy to *Equation 2.26*. Even high

moisture biomass like algae can be used [234, 235], but large quantities will be required for any substantial yields. SCWG can also utilise catalysts, such as potassium/sodium carbonate or ruthenium titanium dioxide, which change the levels of hydrogen productivity, depending on the biomass feedstock and gasifier conditions [230-232]. It can also dissociate any other types of hydrocarbons, including hazardous wastes. Any carbon dioxide and water vapour produced can be separated out using water-gas shift reaction and PSA. When upgrading syngas, this process produces pure hydrogen [236]. However, this is a relatively under-utilised and under-researched pathway, due to advances in standard gasification and liquefaction technologies being more prevalent [237].

2.4. Gaseous By-Products of Liquid Fuel Processes

There are two biomass conversion processes that do not directly produce gaseous products. For completeness, they have been reviewed here, but will be excluded from the analysis conducted as part of this thesis in *Chapters 4* and *5*.

2.4.1. Pyrolysis

This process occurs prior to gasification but is part of both the gasification and combustion processes. This is where the woody biomass is dried to less than 10% moisture content, before undergoing thermal decomposition under very low oxygen partial pressure conditions at supercritical temperatures [238]. The lignin and cellulose is broken down into bio-oil (60%), syngas (15%), and bio-char (25%) [112] (*Equation 2.20*) [81], although it has been found that different temperatures result in different product compositions [239]; Low temperature conditions (<450°C) typically produce high amounts of solid bio-char (charcoal), Intermediate temperatures (~500°C) typically ~35% bio-oil; ~35% bio-char; ~20% syngas, as in [240]), and higher temperature conditions (>800°C) produce more gaseous products, such as syngas.

Biomass + heat → syngas + bio-oil + bio-char *[2.20]*

The bio-oil begins as vapours, which are condensed and collected [241]. The syngas is typically reused within the drying process, for onsite energy. Up to 75% of the bio-char will also be used for onsite energy, and the rest will be sold (e.g. activated carbon market) for additional revenue.

Recent developments of pyrolysis research have made developments regarding different types of lignocellulosic/forestry wastes (including the >60% unused trees and logging residues from the sawmill [116, 212]). For instance, timber rejects (such as beetle infested trees) are becoming an ideal feedstock choice [242-244]. The bark and outer layers of these trees dry out, inhibiting nutrient uptake and causing the trees to starve [245]. Due to the spread of these beetles, and the nature of the fungus they carry, mass tree deaths have resulted in unsafe, unusable wood that cannot be sold within the logging/timber industry. However, due to how the fungus affects the infested trees, the wood has a reduced moisture content; therefore, this waste stream could be repurposed for bio-oil production [242, 243, 246] as it would need less/no drying prior to pyrolysis.

2.4.2. Liquefaction

Wood biomass is transformed into bio-oils/ash using methanol and water under superheated, pressurised conditions [247]; also known as hydrothermal liquefaction. The methanol breaks down lignin so that the water may break it down further, before being separated into bio-oil once stabilised [248, 249]. Like pyrolysis bio-oil, it can be steam reformed into hydrogen and carbon monoxide, and then water-gas shift reacted into additional hydrogen and carbon dioxide (*Equations 2.20 and 2.22*). However, primarily, it is reformed into liquid fuels, such as diesel, via a distillation refinery. The fuel quality produced is like that of fossil and pyrolysis oil, which makes it an excellent substitute.

Recent research has investigated new feedstocks for liquefaction, especially for advanced techniques of hydrothermal liquefaction. Algae grown for biomass yields is growing in popularity, as it can be grown intensively (both indoors and outdoors), utilising agricultural wastewater to fulfil water, carbon dioxide, and nutrient demands [120-122]. However some researchers have found algal biomass can produce high quantities of ash (up to 50%) [250], therefore, further research and development of liquefaction reactor conditions is necessary in order to reduce this by-product.

2.5. The Fuel Cell Spectrum: A Brief Overview

Fuel cells use a variety of fuels, commonly hydrogen, to produce electricity, water, and heat [251] with air typically being the oxidant. They are modular units, built in a variety of sizes and types, but the principal behind each of them is the same [251]: a fuel cell is made up of a fuel electrode with an oxidation catalyst (anode), and an air electrode with the oxygen reduction catalyst (cathode), both sides separated by the electrolyte membrane (*Figure 2.10*).

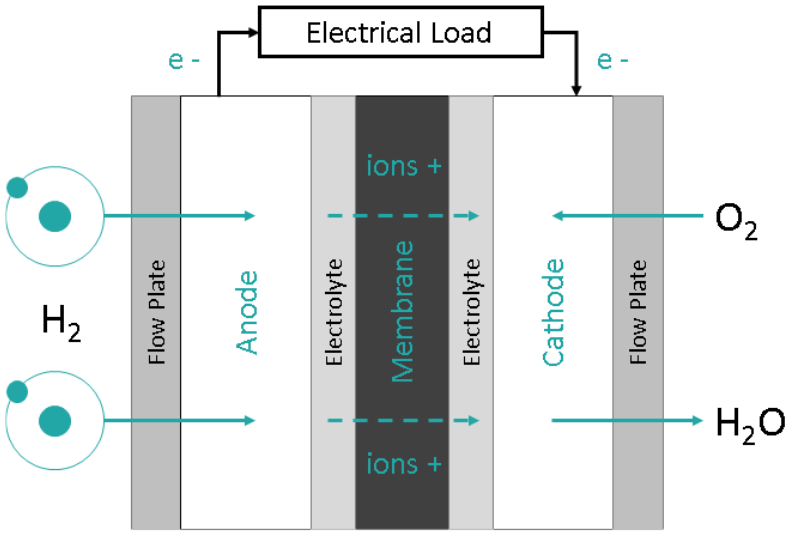

Figure 2.10: The inner workings of a fuel cell
Adapted from: [251]

Fuel cell electrochemical processes occur on the electrode-membrane interface (triple phase boundary – the region of contact between the electrolyte, electrode, and fuel gas

[252]). Output is therefore dominated by the total surface available for reactions. To increase the output of the fuel cell, the accessible surface area of the electrodes must increase, both by increasing the overall geometric size and the catalyst surface (e.g. introducing nanoparticles). The catalysts within the anode and cathode adsorb and electrochemically split the fuel and oxygen molecules, sending electrons to an external circuit, thus producing an electrical current. The ionised species produced pass through the membrane, to the opposite electrode. In the hydrogen fuel case, this solely produces water, being removed from the fuel cell as water vapour.

There are many different types of fuel cells that could be explored in the latter half of this thesis (*Chapters 4 and 5*). *Figure 2.11* illustrates the temperature ranges of the different fuel cells and their ionic charge carriers, assuming hydrogen fuel.

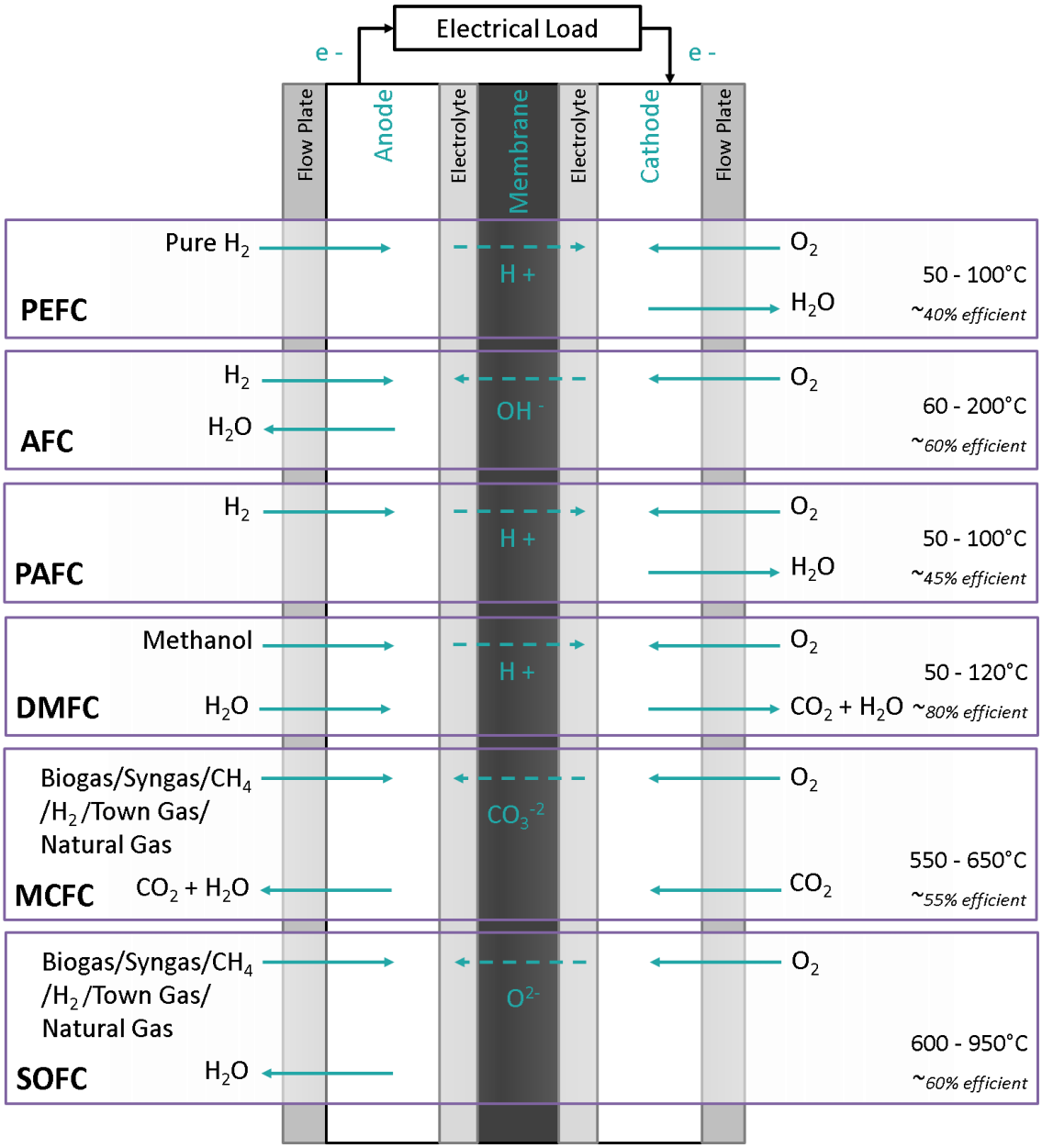

Figure 2.11: Overview of fuel cell technologies, fuel inputs, outputs, operating temperatures, and efficiencies.

Data and Diagram modified from: [251, 253-255].

Notes: (a) AFC efficiency relates to operation on pure oxygen, the others to use of air (21% oxygen).

(b) MCFC can only operate on hydrogen if a separate carbon dioxide feed is provided to the cathode.

2.5.1. Polymer Electrolyte Fuel Cell

This is one of the most employed low temperature fuel cells, due to its compact size and relatively high volumetric and gravimetric output capacity. Polymer electrolyte fuel cells (PEFC) have a solid polymer membrane electrolyte and a platinum catalyst, which is susceptible to carbon monoxide contamination [253]. Due to this, PEFCs can only use pure hydrogen to produce electricity, heat, and water at ~80°C [256]. PEFC are predominately

employed in mobile applications such as most all current fuel cell vehicles, but also in uninterruptible power supply units, as well as stationary applications in domestic and industrial environments [257].

2.5.2. Alkaline Fuel Cell

This is a fuel cell with a potassium hydroxide electrolyte, and a nickel non-precious metal catalyst. Alkaline fuel cells (AFC) produce electricity, heat, and water from hydrogen and oxygen at ~60°C [256]. They were predominately used by NASA for space shuttles, and are still used in space flight today [258].

2.5.3. Phosphoric Acid Fuel Cell

This fuel cell has an electrolyte made of liquid phosphoric acid (H_3PO_4), for instance suspended in a silicon carbide matrix, and carbon-supported platinum catalyst. Phosphoric acid fuel cells (PAFC) generate electricity, heat, and water from hydrogen at ~200°C [256]. They are predominately used for stationary applications.

2.5.4. Direct Methanol Fuel Cells and Use of Liquid Fuels

PEFC do not only operate on hydrogen but can also be run on alcohol based fuels. Direct methanol fuel cells (DMFC) internally produce hydrogen by reforming alcohols at ~80°C operating temperature [256], with an output of electricity, heat, water, and carbon dioxide. There are also variants of DMFC's, such as direct ethanol fuel cells (DEFC) that run on ethanol, and SOFCs that can run on liquid ethers, which are produced from fuels, such as fossil diesel and kerosene, and biodiesel [259, 260]. The anode within the fuel cell cannot handle the liquid fuels in their original state due to their sulphur and carbon contents; methane, methanol, and methanoic acid are preferable.

Alternatively, renewable hydrogen can be produced through the steam reforming on biodiesel, whilst also utilising the glycerol and wastewater by-products from the transesterification process [261, 262]. This method would provide an alternative for steam reformed natural gas, which (albeit being cheap) is not a sustainable source of hydrogen.

Additional research in recent years has been undertaken in running fuel cells directly with liquid fuels. In 2015, Zhu *et al.* [263] published a paper on running PAFC's with liquid fuels, with experiments on anode treatment and performance recovery. One of the key findings was that by treating the anode with water to remove the carbon forming on the anode surface, it removes the need to add water into the fuel cell as part of the reaction; therefore eliminated the need for a water feed system [263].

Prior to this, McPhee *et al*. [264] published similar research in 2009, demonstrating an SOFC with a liquid-tin anode running on biodiesel. Their key findings were the new anode was able to successfully operate on biodiesel and produce commercial viable electricity generation with overall fuel efficiencies at over 40% [264].

2.5.5. Molten Carbonate Fuel Cell

Molten carbonate fuel cells (MCFC) have an electrolyte made of alkali carbonate (Na/K in a ceramic matrix of $LiHO_2$) and a nickel catalyst. They operate on, amongst others, town gas, syngas, natural gas, biogas, methane or hydrogen, just as the SOFC, at 550 to 650°C [256]. They can be used for stationary power, as well as CHP generation from 250 kW_{el} upwards [265].

MCFCs are the only fuel cell that requires carbon dioxide as part of its gas supply. This is due to the use of carbonate ions in the electrochemical reactions occurring within the cell. However, this also provides MCFCs with an advantage, as they can be integrated with

power plants to re-use emitted carbon dioxide [266, 267]. Alternatively, the carbon dioxide from the exhaust gas can be recycled in a closed loop. Since MCFCs operate at high temperatures similar to SOFCs, they produce high quality heat that can be used in CHP or steam generating schemes [266, 268, 269].

2.5.6. Solid Oxide Fuel Cell

This is a ceramic fuel cell that has a high temperature and a lower temperature variant. It has a solid ceramic electrolyte, non-platinum catalyst, and operates on inputs of: syngas, natural gas, biogas, methane, or hydrogen (amongst others) at ~650 to 800°C [256]. Logically, if the fuel gas contains carbon, the fuel cell will emit carbon dioxide. Low temperature variations of SOFCs run at 500 to 650°C. They lose the potential of internal reforming and will need to be operated on hydrogen or syngas [255]. SOFCs are currently predominately used for CHP in domestic and industrial applications [270, 271], as well as auxiliary power units on vehicles.

2.6. Conventional Fossil Hydrogen

As seen in *Section 2.5*, most fuel cells operate on hydrogen; either pure or using hydrogen rich gases such as methane or syngas (hydrogen and carbon monoxide). However, hydrogen is not a common, naturally occurring gas that can be harvested. It must be manufactured. The current commercial method of producing hydrogen is steam reforming of natural gas (methane), or processing syngas in a water gas shift reaction to produce more hydrogen from the carbon monoxide. Both processes are well established and can produce cheap, competitive hydrogen.

However, both natural gas and syngas are currently reliant on fossil fuel resources. Cheap natural gas reserves are depleting, with further explorations into shale gas increasing gas prices, and syngas is produced through coal combustion; another fast depleting resource.

On the other hand, there are alternative substitutes to both of these gases, as previously explored in this chapter. Biomethane can be produced from anaerobic digestion, and syngas is a by-product from gasification and SCWG of wood; three common biomass conversion methods that are becoming increasingly accepted within industry. It is imperative that renewable, sustainable, and biological substitutes for resources made from fossil fuels are explored and supplied for proper market integration and infrastructure expansion.

2.7. Biomass and Fuel Cell Review Conclusions

This review has identified biomass derived products and the extent of biomass research in the last decade. Potential resource and energy solutions suitable to fulfil the needs of society and political commitment for clean, sustainable development have also been explored.

This chapter has found the following:

i. With the increased utilisation of biomass, further development of the capable technologies have been demonstrated, including the increased accessibility of cleaner resources outside of fossil fuels
ii. Fermentation, anaerobic digestion, and gasification have been identified as the most utilised technologies, due to their longevity and practical performance.
iii. SCWG and metabolic processing of algae are the most underutilised techniques, predominately due to the previous mentioned techniques superseding them and being a preferable choice.
iv. A variety of fuel cell technologies have also been investigated, each demonstrating a variety of gaseous fuel choices and applications.

v. SOFCs demonstrated the greatest range of fuels and large scale applications, including future progression to direct use of liquid fuels.

vi. PEFCs have been identified as the most robust fuel cell in terms of small scale and mobile applications, with consumer products utilising this technology (*e.g.* fuel cell cars).

vii. Recent research has demonstrated the future development of these fuel cells for more direct liquid fuel uses and their potential as alternative sources of sustainable hydrogen.

The recovery of gaseous and liquid fuel resources from biowastes has allowed movement towards greener transport and energy sectors. Recent research has been predominately on the technological development and increasing the process efficiencies and yields. What is lacking are comprehensive, thorough assessments of these technologies, and their products, in all-encompassing studies. For instance, there are many LCA studies in these fields, however very few of them provide the transparency, clarity, and depth that is required for these research areas to progress.

CHAPTER 3

This chapter contains content from a publication by S.A. Archer, with the auxiliary editorial feedback from R.J. Murphy (University of Surrey) on how to properly conduct life cycle analysis, and editorial feedback from R. Steinberger-Wilckens (University of Birmingham), which was published under open access (CC-BY 4.0).

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CHAPTER 3. UNDERSTANDING LIFE CYCLE METHODOLOGY

3.1. Background

Life Cycle Analysis (LCA) is a holistic and versatile method of environmental assessment that has developed a wide set of definitions and modes to encompass a variety of specialisations, which are covered in detail by Guinée *et al*. and Kirchain Jr *et al*. [272, 273]. There are a multitude of roles and applications that can utilise LCA: benchmarking products, management strategies, marketing, policy planning, environmental labelling, and corporate governance, to name a few [274]. Regardless of which, it is important to start all LCAs with a key question that is answered during the assessment for it to be verifiable [272]. The most accurate and relevant studies produce robust results, which can be directed at two different targets: policy and regulation. The assessment can be targeted at an aggregated audience, unit process analysis, and product/process improvement, which can utilise different data methods.

As the introduction of waste, carbon, and resource management is becoming a growing concern within politics, LCA is growing in popularity, both for industrial and governmental parties [273]. The first environmental impact studies were produced in the late 1960s [275], but were not extensively utilised until the 1970s, producing energy studies for industrial systems during the oil crisis [276]. In the 1980s it was predominantly an inventory based methodology, transitioning to more environmental impact orientated methodologies in the 1990's [277].

The International Organisation for Standardisation has released a series of international standards for environmental management, which include: ISO 14040 and ISO 14044. These documents cover the practice for LCA and how to undertake all four sections: Goal and Scope, Inventory Analysis (LCI), Impact Assessment, and Interpretation, alongside general

requirements and guidelines [278, 279]. The LCA methodology was created as a decision making tool [280] to support governments, and before that companies, such as Coca Cola [281], in the assessment of potential environmental impacts of their products, activities or decisions. It was also introduced into product design, development, and manufacture, alongside other applications. It also inspired the creation of the 'Greenhouse gases, Regulated Emissions and Energy use in Transportation' (GREET) model by Argonne National Laboratory, which is specifically for the assessment of motor vehicles and their emissions [273, 282, 283]. The process of actually completing an LCA is elaborate; as the field and depth of the study is increased, the complexity will increase considerably [284].

3.2. Methodology Variations

The initial data collection for any LCI analysis can be done through a comprehensive literature review. This involves a time intensive process of extracting data tables from published studies in order to build the data set inventory. However, the reliability of published data across different papers assessing the same field has been found to vary. Therefore, the true extent of their consistency is questionable (see *Section 3.4* for the full assessment), which directly affects the veracity of impact assessment results thereafter.

Once an Inventory has been produced, it can be used to drive the Impact Assessment, as inputs and processes typically use resources and energy, and outputs emit emissions that can affect the air, ground, or water; all contributing to the resulting environmental impacts. Similarly to LCA databases, there are multiple types of Impact Assessments, mostly depending on geographical region (CML-IA Baseline and ILCD 2011 Endpoint/Midpoint – Europe; TRACI 2.1 and GREET– North America; and ReCiPe – Global; full description available in the ILCD Handbook [285]), most of which are available within LCA software, or are compatible with Microsoft Excel/spreadsheets by downloading the data sets. The

primary difference between Impact Assessment methods are the impact categories, as some schemes have more than others, but most methods have the same overarching categories: Resource Depletion, Global Warming, Human Health, Terrestrial Health, Aquatic Health (including Eutrophication), and Acidification [285].

Table 3.1: Typical LCA methodologies, their impact assessment categories, assessment types, and specific model features/applications

Method	Impact Categories	Assessment Type	Specific Model Features/Application
Most Typically Used Methods	*At least three impact categories need to be applied*	• *Whole system* • *Specific product*	• *Geographic applicability* • *Normalisation and weighting factors*
CML-IA Baseline	• Abiotic Depletion • Abiotic Depletion (Fossil Fuels) • Global Warming Potential • Ozone Layer Depletion • Human Toxicity • Freshwater Aquatic Ecotoxicity • Marine Aquatic Ecotoxicity • Terrestrial Ecotoxicity • Photochemical Oxidation • Acidification • Eutrophication	Most generic assessment type for all assessment types. Also utilised in other methods as an integrated model (CML-IA Non-Baseline – same system with multiple time scales; and the lesser used model IMPACT 2002+)	• European issues, • Normalisation and weighting are applied
ILCD 2011 Midpoint	• Climate Change • Ozone Depletion • Human Toxicity, Cancer Effects • Human Toxicity, Non-Cancer Effects • Particulate Matter • Ionising Radiation, Human Health • Ionising Radiation, Ecological (interim) • Photochemical Ozone Formation • Acidification • Terrestrial Eutrophication • Freshwater Eutrophication • Marine Eutrophication • Freshwater Ecotoxicity • Land Use • Water Resource Depletion • Mineral and Fossil Resource Depletion	Product, Resource and Waste Management specific assessment	• European issues • Normalisation and weighting are applied • Released by the European Commission, Join Research Centre in 2012.
TRACI 2.1	• Ozone Depletion • Global Warming • Smog • Acidification • Eutrophication • Carcinogenic's • Non Carcinogenic's • Respiratory Effects • Ecotoxicity • Fossil Fuel Depletion	Tool for the Reduction and Assessment of Chemical and Environmental Impacts	• Strictly for US and Canadian issues • Normalisation and weighting are applied • Buildings, technologies, and products assessment

Table 3.1 (continued): Typical LCA methodologies, their impact assessment categories, assessment types, and specific model features/applications

Method	Impact Categories	Assessment Type	Specific Model Features/Application
Most Typically Used Methods	• *At least three impact categories need to be applied*	• *Whole system* • *Specific product*	• *Geographic applicability* • *Normalisation and weighting factors*
GREET	• Greenhouse Gas Emissions	Energy use and emissions outputs from vehicles operating on different fuels; from raw materials mining, and vehicle disposal.	• Mostly used in US • Specifically used for GHG assessments
ReCiPe Midpoint / Endpoint (E/H/I)	**1) Damage to Human Health:** • Particulate matter • Tropospheric Ozone Formation (Human) • Ionising Radiation • Stratospheric Ozone Depletion • Human Toxicity (Cancer) • Human Toxicity (Non-Cancer) • Global Warming • Water Use **2) Damage to Ecosystems:** • Freshwater Ecotoxicity • Freshwater Eutrophication • Tropospheric Ozone (Ecological) • Terrestrial Ecotoxicity • Terrestrial Acidification • Land Use/Transformation **3) Damage to Resource Availability:** • Marine Ecotoxicity • Mineral Resources • Fossil Depletion	• **Endpoint:** 3 categories • **Midpoint:** 17 impact subcategories • **E:** egalitarian -long term model • **H:** hierarchist (default) – consensus model • **I:** individualist – short term model	• European and World issues • Normalisation and weighting are applied • Applied environmental scores to emissions and resource extractions impacts

3.3. Databases: Filling the Gaps

To maintain true transparency and accuracy, LCA databases can be used to fill gaps in inventory data sets (Table 3.2). There are professional databases, typically available through LCA software (Gabi and SimaPro), which have a comprehensive collection of data for products, processes, energy generation, and wastes. Although not everything conceivable is available, most of the components required to make new product systems

are and can be manually compiled. Individual data sets can also be downloaded (if available) to either assess products within free LCA software (OpenLCA, which comes without databases), or Microsoft Excel/spreadsheets. Due to the sheer extent of the evolution of different software in this field, and their availability, it is not feasible to discuss them all in comparative detail within this thesis. There are several review papers available that discuss and compare a number of different LCA software types; the University of Surrey produced a European specific LCA comparison in 1997 [286], and a more recent report from 2017 by Dovetail Partners provides a more up to date review on the different software choices [287].

The majority of published LCA studies utilise LCA software as they provide extensive LCI data sets and have a built-in Impact Assessment process, therefore results are consistent, even across multiple studies. However, LCA Software does come with its own issues. For instance, the built-in data sets typically take two years between updates, due to the time intensive processes that are required to build these data sets, and if there are uncompleted studies/analyses that are still being worked on when an update is released, it can cause errors if older versions are no longer being supported. Therefore, the affected inventories may need to exchange the unsupported data for newer version(s), or even be completely remade if the update has made major changes in the database. These discrepancies in data availability also demonstrate the importance of calculating and/or producing the key inventory data yourself, and only utilising the databases for large industrial processes and machinery; data that would not normally be possible to collect.

3.4. Methodological Core Phases

Within each of the different methods used in LCA, there are key phases that need to be completed for it to be an acceptable study (*Figure 3.1*) [278]. There are digressions

regarding the Interpretation phase, as results analysis predominately takes place in the Impact Assessment phase. Although an LCA does not yet have a legally binding function, its analysis capabilities are invaluable [288, 289].

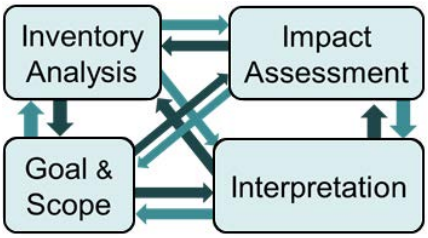

Figure 3.1: LCA phase structure

Modified from: [278]

3.4.1. Goal and Scope, and System Boundaries

'Goal and scope' identify what the study wishes to achieve and defines the functional unit (FU) and system boundary, which are used as parameters in the study's findings. FU's are defined as the key element to every LCA study [278]. They are the unit of reference for the entire system e.g. the total functional input required to produce 1 kg of *X*. They can also be key indicators presented within the study, such as the functional quantity of fuel gas required in order for a fuel cell to produce a specific energy output (*i.e*. kg H_2/MWh). There are also primary units which are used to help calculate a FU, such as an energy input per quantity of produce (MJ/kg). There can be multiple primary units that are used as inputs to generate FU values.

The system boundary is an extremely critical concept in LCA evaluation. It defines the study focus area, within which all the data, and emissions are contained (*Figure 3.2*). *Chapter 4* will demonstrate an LCI case study of biodiesel, providing examples of the main methods and practices involved in data collection and their importance. There are three key intersections that can be utilised: 'Cradle', 'Gate', and 'Grave' for standard systems [278], and 'Well', 'Tank', and 'Wheel' for fuels.

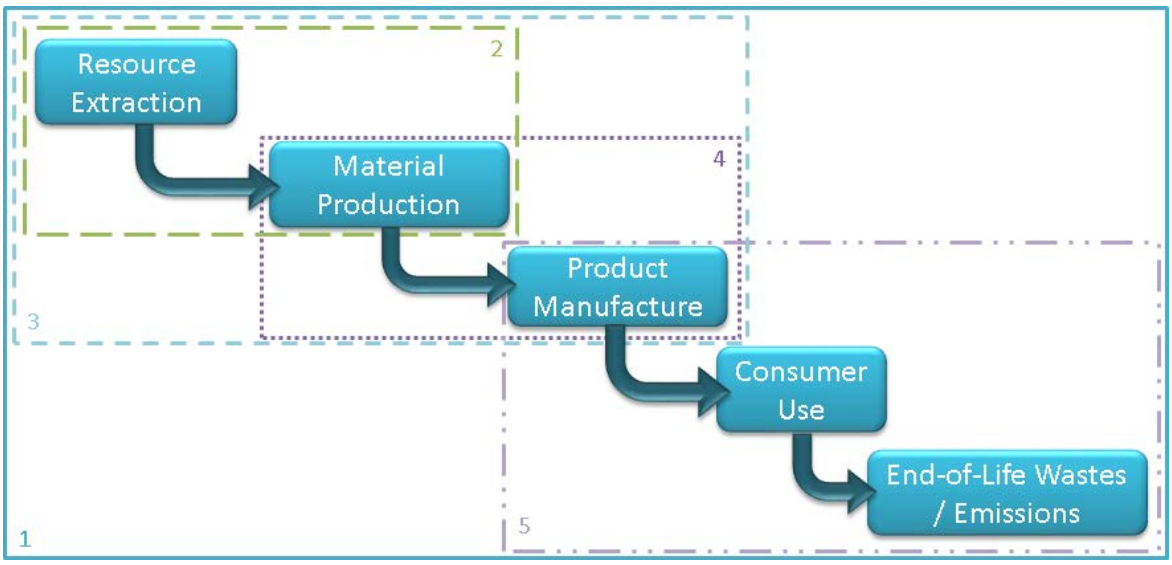

Figure 3.2: Typical LCA system boundaries

Adapted from: [290]

1. **Cradle to Grave / Well to Wheel**: Whole system life cycle
2. **Cradle to Gate 1 / Well to Gate**: Resource origin and processing into a useable material life cycle
3. **Cradle to Gate 2 / Well to Tank**: Resource origin to product production life cycle
4. **Gate 1 to Gate 2 / Gate to Tank**: Product production only life cycle (typical for by-product/waste utilisation)
5. **Gate 2 to Grave / Tank to Wheel**: Consumer use and disposal life cycle

'Cradle' or 'Well' refers to the start of the system, such as a farm or plantation in the case of biomass, or for instance oil extraction from an oil well (hence the term with vehicle fuel analysis of 'Well to Wheel' or 'Well to Tank'). A 'Gate' represents an interface between manufacturing processes, in which 'Gate to Gate' is an LCA of processes only within that industry, not before or after. This system boundary is typical for companies assessing only their responsibility to a specific product, like a catalyst manufacturer whose products are sold on the market for people to buy and use to make their own product. This also applies to 'Gate to Tank'. Between 'Gate to Grave' or 'Tank to Wheel' there are processes, such as the application and use of the end product and any waste disposal/recycling processes (if applicable) which conclude the 'end of use'. One system boundary definition is required for an LCA; 'Cradle to Grave' and 'Cradle to Gate' are the most popular options found throughout many pre-existing studies and cover a specified period of time i.e. 20-25 years. These differentiate studies in terms of the content covered.

There are also allocation and system expansion based assessments, which respectively are the process of either assessing a single product and its by-products and allocating the equivalent emissions per output based on their production ratios (i.e. if A = B + C, and B is 60% of the total outputs, then 60% of the total impacts are allocated to B), or evaluating the environmental impact of a by-product compared to another product on the global market that it would be able to replace.

Industries and companies tend to use different system boundaries to identify global and local emissions [291]. This is because the other production stages are outside their responsibility and therefore outside their realm of influence regarding improvements and sourcing alternative materials [292].

The goal and scope sections allow the reader to fully understand what has been investigated, or excluded, via the system boundary and what the aspirations of the study are. A list of inputs, outputs, and processes (and impact categories with characterisation factors in the impact assessment) are also required for full transparency.

3.4.2. Inventory Analysis and Impact Assessment

The LCI analysis is the most important section of the LCA. It identifies all the quantitative inputs and outputs of the system being assessed, within the chosen system boundary, and provides a list of all processes and products, which are then aggregated into the chosen FU.

Within SimaPro, there are three different types of data, each that apply to two process types. Depending on which data is chosen, the outcomes of the impact assessment will vary (Table 3.2). These choices must also be acknowledged in the goal and scope of the LCA, to allow for methodological transparency.

Table 3.2: Inventory data and process types

Data Set Type	Summary	Process Type	Specific Process Features / Application
Allocated Default	Impacts of all inputs, outputs and processes are allocated to a specified primary output quantity.	• System • Unit	*System Processes:* One single core process encompasses every sub-process under one single list and they are all aggregated to its singular output. *Unit Processes:* Each core process is made up of modular sub-processes, for which each of the input and output data within are aggregated to individual quantities. The core process then specifies how much of each sub-process should be allocated to each of its outputs. *Avoided Products:* Unit Products with recycled content have allocated mass proportionate to the amount of virgin and recovered materials on the market (e.g. 60g virgin, 40g recovered, for a 100g product). These products can lead to negative results (avoided impacts) due to the avoided virgin materials.
Allocated Recycled Content	Avoided impacts are factored into the data sets for parameters with recycled content, which reduces the demand on virgin resources.	• System • Unit	
Consequential Data	A product determined by an overriding functional unit, which when changed the allocation of activities linked to that product system also change .	• System • Unit	

The more complete this list is, the greater the value of the impact assessment (as found in *Section 3.5*), which determines any potential impacts and hazards using impact categories (*Table 3.3*), such as Global Warming Potential over 100 years (GWP^{100a}), Eutrophication, and so forth [1, 285, 293].

The purpose of these impact categories is to reduce the number of key parameters by grouping many different emissions and impacts together, as a complex inventory could potentially include thousands of data inputs. Some categories have pollutants with greater levels of impacts, as defined by their greenhouse gas potential, which is measured in relation to carbon dioxide. For instance, methane has a greater impact per kg than carbon dioxide, by a factor of ~25 [1, 294, 295]. This is due to methane absorbing more heat (infrared energy) than carbon dioxide, which accelerates warming. There are also different

values for methane, depending on how far ahead the study is looking, as it does not stay in the atmosphere for as long as carbon dioxide [294-296].

Table 3.2: Examples of LCA impact categories, the driving pollutants, their heating potential, emission units, and resulting environmental impact

Sources: [1, 285, 290]

Impact category*	Dominant emissions (and their heating potential in relation to CO_2 for GWP)	Emission Unit	Environmental impact
Global Warming Potential (100 years)	CO_2 (x1) N_2O (x298) CH_4 (x25)	*Kg $CO_{2\ eq.}$*	Climate change
Eutrophication Potential	NO_3 P NH_3 NO_x N	*Kg $NO_{x\ eq.}$*	Reduced water quality, algal blooms, and decreased biodiversity
Acidification Potential	NH_3 NO_x SO_x	*Kg $SO_{2eq.}$*	Health impacts and ecosystem damage
Abiotic Depletion (Fossil Fuels)	Coal Natural gas Crude oil	*$MJ_{eq.}$*	Fewer fossil energy resources for future use

* Typically, within CML-IA Baseline Impact Assessment methodology, but some categories are also found within other Impact methodologies (*see Table 3.1*).

These impact categories must all be assessed from comparable data sets, which allow impact assessments to be compared across studies. The ISO 14040 and 14044 standards must be used in conjunction with each other, preferably not stand alone, in order for studies to be recognised as official LCAs; they must also be critically reviewed in order to ensure authenticity [297]. In order for the LCA to abide by ISO 14040 and 14044 standards, *at least three* impact categories have to be assessed [298].

It is also important for all data collection methodologies and results generated with intent to compare to be conducted with identical reporting categories, and procedures to abide by ISO 14025 [299]; for instance:

- A list of impact categories to be considered must be specified and applied to all pathways assessed
- The data types and processes must be consistent across each pathway assessed
- The details of the LCA must compliment the ISO 14044 standards; *i.e*. more than three impact categories, utilises the four phase structure, comparable system boundaries, *etc*.
- Any public claims must be backed up by a comprehensive LCA, reporting on all impact categories applicable to the product/system; *i.e*. an in-depth analysis, not a single issue assessment.
- Correct use of Functional Units and Reference Cases
- Weighting factors are not applicable to comparative studies, and they introduce too many inconsistencies.
- All process calculations are to be incorporated between the LCI and LCIA phases, to produce more comprehensive results.

ISO 14025 recommends an iterative process, which instead of the final interpretation phase, each of the three phases (Goal and Scope, LCI, and LCIA) are evaluated individually against the original Goal and Scope to ensure that what methods have been stated have been fulfilled. An additional assessment of what is driving the impacts (sub-process/substance contribution analysis) is then recommended instead of the interpretation phase.

3.4.3. Results Discussion and Impact Contribution Analysis

The final phase contains an analysis of the results from the previous sections, identification of 'hot spots' (significant issues), the sensitivity of data (change in results when input data are varied), and draws a conclusion for the study, describes its limitations, and provides

recommendations towards improvements for decreasing any environmental impact, using the emission indicator values. The results can be compiled into a format that is easily understood, usually consisting of graphs and charts with explanatory statements, comparisons, and conclusions.

In all cases, a reference case or benchmark is required. This will most often be the incumbent technology, such as fossil fuels. For instance, if the result for GWP^{100a} is either neutral (0) or negative, this would be considered a positive outcome. If it is higher than the fossil fuel equivalent which it is intended to replace, the technology assessed has failed, if GWP^{100a} reduction was its aim. This method is approved at an international scale, highlighted in the LCA guidelines within ISO 14044.

There are issues of comparing studies that have used methods of weighting impact categories, which is where impact assessment results are multiplied by a weighing value (which varies dependant on the weighting method) in order to adjust the results to show 'more relevant' categories, but each study might choose different categories of significance. It is recommended that weighting should not be included in comparative LCA studies, which are to be published. This is due to the potential of misunderstanding of any results and/or estimate [300], which would be inaccurate if compared against other unweighted results.

However, for studies to provide in-depth individual conclusions it is recommended that each study needs to complete a substance contribution analysis. This will isolate the driving emissions/impact sources. In addition, there is also the method of data normalisation, which involves dividing the characterisation data by a normalisation factor (specific values depend on the method used) and produces a dimensionless value, across all impact categories, allowing them to be compared directly. The normalised impact assessment

results convert from the standard impact category specific units to an 'EU domestic' unit, equating impacts to 'per person per year' equivalence [301] and demonstrates the personal magnitude of impacts [302]. This method allows low quantity, but potent, impact categories to be equally represented.

Unfortunately, apart from the 'critical review', there is currently no assertive presence from the International Organisation of Standardisation to ensure these guidelines are followed. Many studies slip under the radar during publication due to ISO standards only being conventions, not laws that can be policed [289, 300]. This causes LCAs to vary considerably due to methodological discrepancies, which is investigated in *Section 3.5*.

Concerning the inconsistencies in studies found in literature, the most common methods to highlight differences will be a systematic review, to identify where the causes of the variations in assessment conclusions originate. This is presented in the palm oil biodiesel case study.

3.5. The Palm Oil Biodiesel Enquiry

In order to properly understand LCA, peer reviewed journal papers have been assessed as part of a life cycle methodology case study; specifically, POBD as it is a highly researched field. It is important to recognise that considerable scope remains for transparent and unbiased methodologies in Life Cycle Analysis (LCA) studies.

Transparency can be achieved by thorough explanation of all processes and methodologies used to achieve the presented results. Studies that exclude areas of the field that should be present without explanation, such as system boundary limitations, and lack objectivity or clarity regarding their results decrease their transparency. Practices such as these struggle to follow the necessary uniformity, which is required for successful comparability

between different LCA studies. Thus, in this analysis, the methodological aspects of Palm Oil Biodiesel (POBD) LCA studies will be explored in order to demonstrate the range of methodological practices in the field; some studies of which have been deemed to fall outside of a helpful application of LCAs inherent flexibility.

The key findings of this research are hoped to help non-LCA-specialist users of LCA studies to assess and recognise more reliable results through stringent checking and of the analysis in any data sets published. This will be especially important when the LCA results will be used within further analysis and comparisons leading up to political strategy decisions.

While undergoing this research, it was interesting to find that studies of supposedly the same topic, with similar scopes, had results of significant variation. Therefore, in order to identify the key drivers of these inconsistencies, which have also been seen in other published topical areas outside of POBD, an in-depth analysis regarding the methods and content of more comparable papers has been conducted to highlight why these papers contain different results for the same topic.

3.5.1. Greener Fuel

Biodiesel is an alternative transport fuel to fossil diesel. It is renewable and can be derived from several feedstocks, such as vegetable oils (like rapeseed and jatropha [303-305]) and recycled waste cooking oil [306], amongst others. The production of biodiesel predominately utilises transesterification to produce a monoglyceride biodiesel (and ~10% glycerol co-product of total biodiesel yield) from plant oil precursors, with more recent movements adding a catalytic hydroprocessing stage [307].

The principal advantages claimed for biodiesel are that it is renewable and, although the 'Tank to Wheel' energy density of biodiesel at 39 MJ/kg is marginally lower than the 42.8

MJ/kg of fossil diesel, its GHG emissions are lower [308-310]: 3 kg CO_2/litre biodiesel versus 3.16 kg CO_2/litre fossil diesel. This includes factors such as feedstock carbon sequestration during growth [311], which reduces the effective emissions, and land use change [312-314], which increases emissions from the soil with increased fertiliser use and soil disturbances during activities such as sowing and harvesting. These are two influential factors for biofuel production, is becoming increasingly important, as they directly contribute to the overall carbon impact of the biodiesel.

There are various review studies that address analysis comparability. Bessou *et al*. [315] reviewed 70 biodiesel LCA studies, grouping similar work in regard to feedstocks (palm oil, jatropha, sugarcane *etc*.), and highlighted LCA parameter information such as geographic location, functional unit (e.g. 1 kg or 1 MJ or 1 tonne Palm Oil Mill Effluent (POME) *etc*.), system boundary (cradle to grave/gate/tank *etc*.), and which impact assessment criteria was used (CML-IA/IPCC 2006/Energy Balance *etc*.) [315]. Malça *et al*. [304] conducted a similar study with 28 comparative biodiesel LCAs, including their own study. It covered information such as the type of LCA method (attributional), whether Indirect/Direct Land Use Change was included or not, energy requirement, GHG intensity, as well as geographic location, to name but a few. A meta-analysis was published in 2012 by Manik and Halog [316], who reviewed a number of palm oil LCA studies, focussing specifically on impact assessments and energy balances. Another comparative study is by Rocha *et al*. [317], who compared 12 Brazilian biodiesel LCA studies, five of which were from soybean and five from palm oil feedstocks.

3.5.2. A New Perspective

This case study presents the Life Cycle Inventory (LCI) data set summaries side by side, comparing studies regarding completeness, since some papers did not display data for all

the parameters listed. Regarding these comparison studies for biodiesel LCAs, few papers include details on whether the study complied with the ISO LCA standards, and none of the papers were explicitly clear about which LCA approach is used: consequential (a decision based product life cycle model that focuses around an interlinked system that is determined by a functional unit, and change with the demand for it); or attributional (value and supply chain models where inputs and outputs are attributed to a functional unit according to interlinked activities or physical properties) [318].

There are variations in the way that reports are presented from large organisations like the Royal Society, UNEP GEF, IFEU, WWF *etc*. and research/production boards like the Roundtable on Sustainable Palm Oil, as some will only look at carbon or energy, and rarely quantitatively. On the other hand, there are increasing efforts across multiple research fields in aligning divergent studies and normalising them, so that the results can be presented in a comparable and calibrated manner [319]. This was addressed by Farrell *et al*. [320] through normalising LCA data to gain an overall understanding, as well as by Manik and Halog [316].

The above considerations formed the basis for the exploration of possible ways to assist non, or less specialist users of LCA to interpret the environmental profile outcomes of different LCA studies. By providing a perspective on the structuring of LCA frameworks, this chapter intends to provide some significance to this research field, focusing on comparative assessments of environmental assessments.

Biodiesel production from palm oil was selected for this examination because it is a mature process and, as a highly productive and well-established crop system, palm oil offers much future scope for further generations of biofuels, bioenergy and bioproducts. Calibration of results and assurance that the environmental profiles of such palm oil products meet

sustainability requirements will be a key component of any policy and investment decisions concerning the future development of palm oil and other biomass-based systems.

From an initial collection and overview of biodiesel-based papers, as input to the analysis presented here, over 100 studies were relevant to palm oil, from these, 17 studies with adequate inventory data were selected, out of which only 11 had sufficient breadth of coverage of the palm oil supply chain, relevance to POBD, and had been published in refereed, archival journals. Having located several review articles on palm oil with only four to eight studies, 11 studies were found to be adequate for the research's purpose. These were analysed to evaluate the reasons for variation regarding the results of their LCI, and consequently their Impact Assessments.

Having selected POBD as an exemplary topic, the objectives of the in-depth study were:

i) To develop a generically-representative LCI data set of a 'Well to Tank' POBD system (from palm oil biomass production to biodiesel production, ready for use) based on available published inventory data within literature.

ii) To explore and assess the data extracted from the studies and discuss the variations found across published data in the literature.

iii) To explore the variance of LCI outcomes, focusing on discrepancies in specific parameters.

iv) To examine how methodological and other choices could affect the outcomes of POBD studies.

3.5.3. Materials and Methods

To fulfil mentioned objectives, LCA studies on POBD have been reviewed, and a generic LCI built to reveal sources of discrepancy in published findings and to identify ways of minimising such variation in LCA study outcomes.

i. Selection of Studies

There are multiple strategies that can be utilised to produce a robust LCI data set from published data. There are two commonly used methods: systematic review (a methodical reference standard for producing evidence under pre-specified eligibility criteria); and meta-analysis (a statistical analysis combining and summarising multiple studies) [321]. In practical application, systematic reviews are utilised to help identify research with results that are consistent with a set of assessment criteria. These are commonly used alongside decision trees, which help to visualise the criteria assessment process. Meta-analyses are used for comparative studies, producing augmented data that can summarise the range of data across these studies. This method is also used in parallel to harmonisation, which is where data is combined across several levels to produce a single data set.

For this study, a systematic review was conducted to identify appropriate sources from literature published between 2007 and 2018, using online resources such as ScienceDirect, Scopus, and official journal websites, including but not limited to Elsevier and Springer, to enable development of an augmented, generic LCI for POBD based on a meta-analysis approach. Unfortunately, there were no useful studies found from 2015 onwards that could actively contribute to this assessment. Most papers were missing key data outputs, and/or contained data very similar to those already investigated, and so would not add anything new at this time. Despite these issues, LCA software and databases were not used for this study and instead relied solely on the reported data, just as any potential user of

this literature would have to do. As a result, a production system analysis was adopted, from an established plantation through to biodiesel production, but not biodiesel use.

ii. Decision Tree

During background research, it was found that many papers whose titles suggested relevance to LCA of biodiesel were either unrelated to palm oil [322-324], had incomplete data sets [325, 326], or were incompatible with other studies - typically due to data that could not be augmented or varied substantially in terms of parameters, system boundaries, and/or data coverage. These variations limited their value for assimilation into a generic data set, especially due to rather few studies having consistent data fields. The decision tree in *Figure 3.3* was used to determine the suitability of a published article for use in this research.

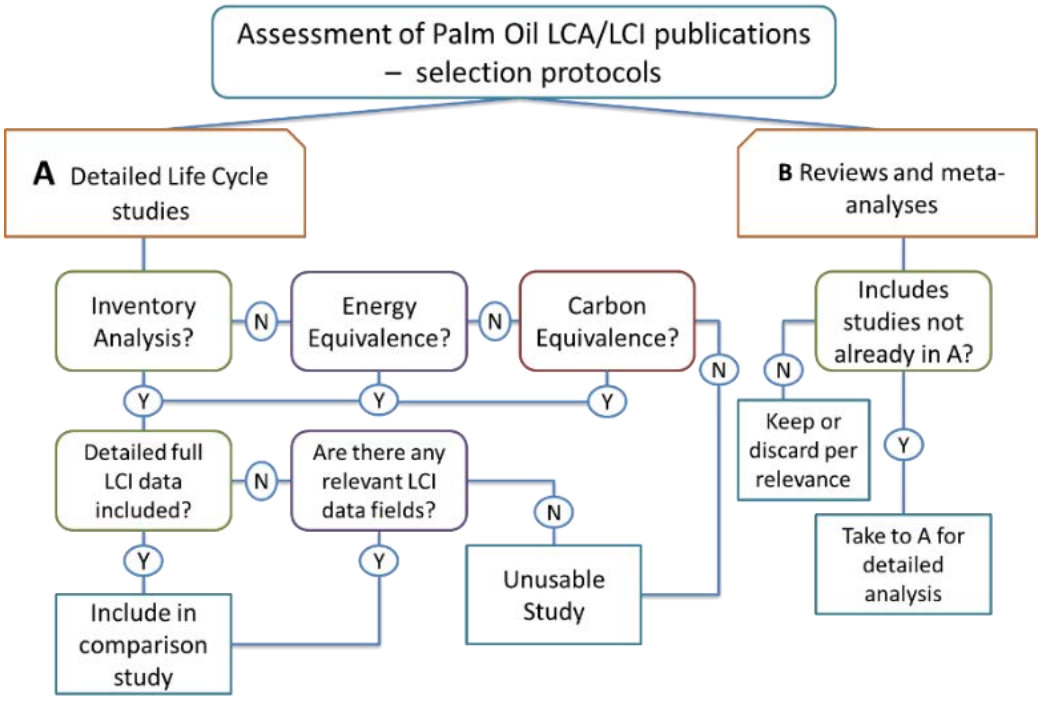

Figure 3.3: Palm Oil LCA/LCI publications for comparison analysis - identification and selection decision tree.

At the highest level in *Figure 3.3,* papers and other publications were reviewed for their methodological basis and the comparability of inventory data within the overall goals of this study. Articles passing this high-level filter were then considered under either 'Route

A' or 'Route B'. 'Route A' represents research papers with 'complete' published inventory data sets and, depending on the information content, relies on how compatible they were with other relevant studies for LCI and overall LCA evaluation. 'Route B' addresses review articles and meta-analyses of the subject area. These were useful for data and augmented outcomes and as sources of additional studies for individual analysis under 'Route A'.

Table 3.3 identifies the countries of origin of the investigated studies and whether LCA environmental impacts/an energy balance were included in the results. In the initial meta-analysis, 150 studies were identified to cover relevant research topics but, within these, only 17 studies [82-86, 325, 327-337] had a suitable level of transparent data sets. *Table 3.3* also lists the three types of LCI data and Impact Assessment categories covered within each study. The categories, based on the ones listed in LCA database software such as SimaPro and Gabi, which some studies used, use a variety of impact assessment methodologies, including CML-IA baseline, ILCD 2011 Endpoint/Midpoint, and ReCiPe.

Alternative impact assessment methodologies differ through which impact categories, and/or resource/emission contributors are used. To cover all impact methodologies, the categories were aggregated under the four main areas: Human Health, Ecosystem Quality, Resources, and Land Use Change. Within these categories, the most frequently found data consisted of Global Warming Potential (GWP^{100a}/Climate Change/GHG), Eutrophication Potential, Acidification Potential, Fossil Fuel Resource Use, and Land Use Change; all except the latter are typical of the CML-IA baseline methodology.

In many cases, published papers and reports only cover one critical environmental impact (usually GHG emissions or GWP^{100a}). Only half of the studies in *Table 3.3* assessed the potential impact of land use change; four of which were further assessed in stage two.

Table 3.3: LCI and Impact Assessment content of the papers selected for in-depth analysis

Reference	Study Lead Author	Geographic Location	Comparable	LCI: Quantity	LCI: Energy	LCI: Carbon/Emissions	Human Health: Carcinogens	Human Health: Respiratory Organics	Human Health: Respiratory Inorganics	Human Health: Climate Change/GWP/GHG	Human Health: Radiation	Human Health: Ozone Layer	Ecosystem Quality: Ecotoxicology	Ecosystem Quality: Eutrophication	Ecosystem Quality: Acidification	Resources: Metials/Minerals	Resources: Fossil Fuels	Land Use Change: Decreased Diversity	Land Use Change
[342]	**Costa, 2007**	Brazil	R	R														R	
[343]	**Queiroz, 2012**	Brazil	L	R	R														
[344]	**Souza, 2010**	Brazil	A	R	R	R				R									
[345]	**Achten, 2010**	Cameroon	R	R						R				R	R		R	R	
[340]	**Harsono, 2012**	Indonesia	A	R	R	R				R								R	
[346]	**Nazir, 2010**	Indonesia	R	R			R	R	R	R	R	R	R	R	R	R	R	R	
[97]	**Kamahara, 2010**	Indonesia	R	R	R														
[350]	**Yusoff, 2007**	Malaysia	R	R		R	R	R	R	R	R	R	R	R	R	R	R	R	
[98]	**Choo, 2011**	Malaysia	R	R		R				R									
[347]	**Pehnelt, 2012**	Malaysia	A	R	R	R				R									
[348]	**Wicke, 2008**	Malaysia	R	R		R				R							R	R	
[349]	**Yee, 2009**	Malaysia	L		R	L				R							R		
[351]	**Uusitalo, 2014**	Mixed	A	R	L	R				R								R	
[352]	**Papong, 2010**	Thailand	R	R	R														
[96]	**Pleanjai, 2007**	Thailand	R	R	L	L													
[94]	**Patthanaissaranukool, 2013**	Thailand	R	R	R	R				R						R	R	R	
[95]	**Pleanjai, 2009**	Thailand	R	R	R														

Acceptable A Reasonable R Limited L No Data

Of the papers that did assess land conversion, the majority assumed rainforest – both primary and replanted, cultivated grasslands, and/or peatland [325, 330, 333, 335, 336]. In

addition, only two studies performed every impact category (Nazir *et al*. [331] and Yusoff *et al*. [335]), and a quarter of studies investigated more than two impact categories. Therefore, due to data inconsistencies across most impact categories, Impact Assessment was excluded from this research, as it would be neither beneficial nor impactful to the field. Development of a thorough LCI would be a more novel contribution to the field, as the investigatory research for this study found many of the previously published LCAs focus mostly on their LCA results and are inconsistent in their LCI data methodologies. Therefore, the meta-analysis and LCI aspects of this study were focused on in order to produce a generic LCI, with coefficients of variation, from this literature. This in turn would allow us to analyse the studies and identify their methodological variation outcomes for non-LCA-specialist users. The limitations of this approach are considered in the discussion of this chapter.

The '*Comparable'* column in *Table 3.4* represents an overview of the suitability of the articles' base data and Functional Units (FUs) from a variation of complete to somewhat sparse studies. 'Acceptable' studies contained data that was comparable either directly or through very limited re-calculation or conversion, 'Reasonable' studies covered at least two of the three core LCI data categories but required conversion/data reworking of the energy equivalence data, and 'Limited' studies had data which could not be directly compared despite covering the necessary LCI data categories. This process led to a reduction in the article set down from 17 studies to 11.

Throughout the assessment of numerous articles, it was clear that different publications have different methodological structure within this area of LCA research. As a result, a detailed LCI on POBD was produced, with the aim of delivering a comprehensive model data set. The results gained seek to give insight on the divergence in evaluation and to

develop further understanding of how this variance in results may be mitigated within the LCA approach and methodology.

3.5.4. Development of Generically-Representative LCI Data Set for POBD

The model POBD LCI was developed following the principles of ISO 14040 and 14044 standards [278, 279].

i. Goal and Scope

The aim of the study was to conduct an overview of POBD production, assessing the inputs and outputs throughout the palm plantation, Crude Palm Oil (CPO) processing plant and biodiesel production plant stages. As the use phase was not included, excluding fuel distribution and the combustion phase, the resulting assessment is typical of a 'Well to Gate' analysis.

ii. Functional Units

The Functional Unit (FU) of this study is 'the production of 1,000 kg POBD'. The demands for CPO and Fresh Fruit Bunches (FFB) have been ratioed accordingly to correspond to a reference flow of 1,000 kg POBD. There are three expressions for this study with the following data types:

- **Quantity data: kg/1,000 kg POBD**

This is used within the LCI for input substances, such as fertilisers and herbicides. Quantity values are based on the amount of FFB output, which in turn is determined by the amount of CPO required to convert into the POBD FU. This is due to CPO and FFB being the key ingredients for POBD.

- **Energy equivalence data: MJ $_{eq.}$/1,000 kg POBD**

The quantity of several input substances (e.g. fertilisers, herbicides) is determined by the amount of FFB output, which in turn is determined by the overall 1,000 kg POBD FU. The energy equivalence value for such substances is directly related to the FU, regarding its

energy content, and in the cases of fertilisers and herbicides, the amount of energy required to produce them.

- **Carbon equivalence data: kg $CO_{2\ eq.}$/1,000 kg POBD**

The carbon equivalence of the inputs and outputs is also included in this assessment, but not the combustion of the POBD due to it being outside of this study's system boundary. Like energy, all the carbon equivalence values are calculated on a FU basis.

iii. Data Set Collection, Normalisation and Completion

The individual elements of inventory data were extracted from the 11 studies passing the systematic review and organised under three key stages of POBD production: FFB plantation (Stage 1), CPO processing (Stage 2), and POBD production (Stage 3). Each study presented slight to substantial differences in the quantities of FFB, CPO, and POBD, so all the key LCI data were homogenised so that all studies utilised the same FU. As shown in *Table 3.4,* some studies had only one set or mixed sets of inventory data consisting of quantity, energy and/or carbon equivalence data types.

Studies with only energy and/or carbon equivalence data were used to assist in completing missing fields from other studies, taking care to only use data from similar geographic locations to fill in gaps. Palm Oil can only be produced in certain climatic zones, namely between the latitudes 10 to 20° North and South of the equator [336], so the inaccuracy factor from using data from dissimilar geographies was minimised. As few studies had previously contained all three data types across the chosen fields, this approach was adopted to produce a model process chain as comprehensive as possible. The development of the meta-analysis resulted in an augmented LCI data set that progressed from some of the individually very sparse, incomplete data in any given publication. The data fields chosen were based on frequency of occurrence across the 17 studies. Of these fields, many

studies only contained less than 25% when the three data types were originally extracted from the source publications. These data sets were then augmented and geographically completed up to a level of 95% of the fields. This was achieved by going back to fundamentals, such as carbon equivalence or $MJ_{eq.}$/kg values and completing missing data by using data from geographically comparable studies. For instance, overall energy equivalence and carbon equivalence were calculated using *Equations 3.1* and *3.2*, respectively.

$$\textit{Energy Equivalence } (MJ_{eq.}/kg) * \textit{quantity (kg)} \qquad [3.1]$$

$$\textit{Carbon Equivalence } (kg\ CO_{2\ eq.}/kg) * \textit{quantity (kg)} \qquad [3.2]$$

This resulted in converting what was once 17 sets of incomparable POBD LCI's to 11 comprehensive data sets, which covered quantity, energy, and carbon equivalence in a comparable, consistent format.

3.5.5. Results

The augmented values of the resultant LCI data set of the POBD production process are presented below, together with a detailed presentation of the ranges of results and uncertainties deriving from the individual sources.

i. LCI Structure – Process Overview

To produce 1,000 kg POBD, 5,123.6 kg ±36% of cultivated FFB from the Palm Oil Plantation are fed into the CPO processing stage. Within the CPO plant, the FFB are sterilised in an autoclave for ~90 mins at ~125°C, ~1.37 bar [82, 84]. The fresh fruit is then stripped from the fruit bunches and mashed under steam-heated conditions in a process called 'digestion'. The CPO is extracted, typically yielding an amount of 987.9 kg ±15% as the mashed pulp is pressed, before being centrifuged, purified and stored at 60°C [82, 84]. Additionally, the fibre and nuts are removed from the press. The nuts are then cracked,

separating the kernels from the shells so they can be sold. The fibre and shells can be used as boiler fuel to produce carbon neutral electricity and steam on site [82, 84, 338], due to carbon sequestration during biomass growth. This resulted in allocation of avoided grid electricity during the crude palm oil production stage. An improvement of this could be converting the POME, which is the wastewater from the 'digestion' process, and the Empty Fruit Bunches (EFB) into biogas in an anaerobic digester. This biogas could then be used in a boiler, turbine, or fuel cell to produce electricity and heat (for steam production); which some studies did consider [83, 85, 86, 327, 329, 330].

The CPO is then passed on to the next stage, Biodiesel Production, where conventionally it is transesterified using methanol and sodium hydroxide, to finally yield 1,000 kg of POBD and 110 kg of glycerol, which are produced together [339]. During this process triglyceride oils are converted to methyl esters through the addition of methanol. This reduces the molecular weight to one-third, reduces the viscosity by a factor of eight, and increases the volatility. The methyl esters are then washed, so the glycerol is finally gravitationally separated overnight [338], resulting in a more refined biodiesel product.

The Sankey diagram in *Figure 3.4* provides a graphical representation of this system. It also demonstrates the additional inputs, wastes, and primary/secondary product flows (fresh palm fruits/crude palm oil) to the final stage product, POBD, with its glycerol by-product. Most studies utilised wastes and by-products either for onsite energy or sold them for additional revenue. Some of the studies considered methanol recovery and reuse, but most did not discuss the amount of washing wastewater produced. Therefore, it could be assumed that the water and methanol inputs would equal the washing waste outputs, but with varying degrees of evaporation and potential losses from the system, it was not possible to calculate these amounts.

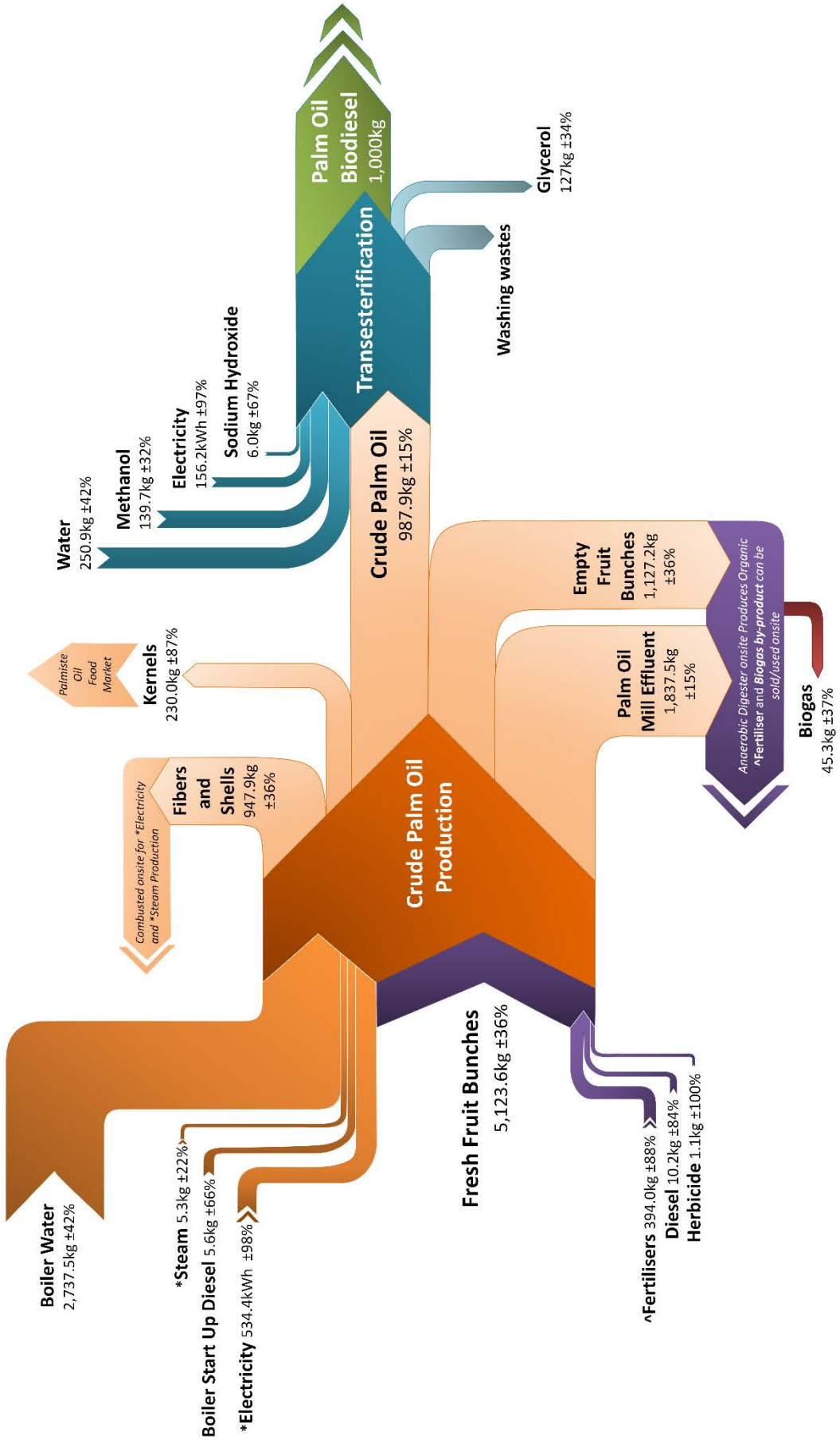

Figure 3.4: Augmented LCI quantity flows with Co-Efficient Variation Percentages, based on 11 LCA study references

Data sources: [82-86, 327, 329, 330, 333, 335, 337]

Figure 3.4 highlights the flow of materials and resources. Inspecting the graph offers some insight into not only the current coefficients of variation between the key studies in this research, but also opportunities for improving the process efficiency. For instance, the amount of water used in the CPO processing stage boiler, for producing steam, is one of the highest inputs within the system, of which most exits the system within the POME. This indicates possibilities of heat recovery and possibly water management.

The CPO processing stage generates several biomass co-products coming from the separation of the FFB. The EFB and POME can be treated in ponds onsite and then used as a substitute for inorganic fertiliser, and the biogas produced from POME could be converted to electricity. Most studies currently use a mix of grid electricity and onsite generation from waste biomass. The fibres and shells are combusted to produce electricity and steam for the CPO processing stage, and the kernels are typically sold on for palm kernel oil production.

ii. Analysis of Variations within Inventory Analysis Data

a) Quantity Data

The quantity data was analysed first, as the energy and carbon equivalence data had to be synthesised based on this data set. The FU was defined as 1,000 kg POBD for all 11 studies and the amount of FFB and CPO were amended accordingly (*Figures 3.5, 3.8 and 3.9*).

The range of data generated varied considerably for certain studies, as demonstrated by the Pleanjai *et al.* [84] study. *Table 3.4* provides a summary of the LCI data generated. For the production assessments in *Figures 3.6* and 3.7, the data in *Table 3.4* was used to calculate a CPO average (1,055 kg/1,000 kg POBD) and an FFB average (5,180 kg/1,000 kg POBD). These values were not used anywhere else except in the variance analysis to demonstrate differences above and below the median data values.

Table 3.4: Augmented Life Cycle Inventory: quantity, energy, and carbon data with medians and co-efficient variation bandwidths.

Data sources: [82-86, 327, 329, 330, 333, 335, 337]

Fresh Fruit Bunches	***Quantity (kg)***			**Co-efficient Variations *(%)***	***Energy Eq. (MJ $_{eq.}$)***			**Co-efficient Variations *(%)***	***Carbon Eq. (kg $CO_{2\,eq.}$)***			**Co-efficient Variations *(%)***
	Median	**Min**	**Max**		**Median**	**Min**	**Max**		**Median**	**Min**	**Max**	
Fertilisers												
N	154.8	7.1	302.5	95	7,513.5	234.7	14,792.3	97	188.8	8.6	369.1	95
P	42.4	0.4	84.5	99	739.5	6.1	1,472.8	99	51.8	0.4	103.1	99
K	126.2	37.3	215.0	70	1,178.1	124.6	2,231.7	89	153.9	45.5	262.3	70
Mg	33.1	2.9	63.3	91	618.8	54.2	1,183.4	91	40.4	3.5	77.2	91
B	37.5	0.4	74.6	99	1,571.0	18.2	3,123.9	99	45.8	0.5	91.0	99
Total	**394.0**	**48.1**	**739.9**	**88**	**11,620.9**	**437.8**	**22,804.0**	**96**	**480.6**	**58.6**	**902.7**	**88**
Herbicide	1.1	0.0	2.2	100	248.7	0.1	497.2	100	11.4	0.0	22.9	100
Diesel	10.2	1.7	18.8	84	538.7	60.3	1,017.1	89	29.9	19.6	40.1	34
Water	8,250.0	8,250.0	8,250.0	0								
Full Bunches	5,123.6	3,255.0	6,992.2	36	78,040.0	52,080.0	104,000.0	33	5,880.7	3,736.0	8,025.4	36
Crude Palm Oil	***Quantity (kg)***			**Co-efficient Variations *(%)***	***Energy Eq. (MJ $_{eq.}$)***			**Co-efficient Variations *(%)***	***Carbon Eq. (kg $CO_{2\,eq.}$)***			**Co-efficient Variations *(%)***
	Median	**Min**	**Max**		**Median**	**Min**	**Max**		**Median**	**Min**	**Max**	
Full Bunches	5,123.6	3,255.0	6,992.2	36	78,040.0	52,080.0	104,000.0	33	5,880.7	3,736.0	8,025.4	36
Boiler Water	2,737.5	1,575.0	3,900.0	42								
Steam	5.3	4.2	6.5	22	6,423.3	2,537.6	10,309.0	60				
Electricity (kWh)	534.4	9.7	1,059.2	98	1,924.0	34.9	3,813.1	98	61.9	6.2	836.8	1,251
Diesel	5.6	1.9	9.2	66	251.7	106.0	397.3	58	18.4	7.8	29.0	58
Empty Bunches	1,127.2	716.1	1,538.3	36	8,205.9	5,213.2	11,198.7	36	805.6	511.8	1,099.4	36
POME	1,837.5	1,553.5	2,121.6	15	305.0	257.9	352.2	15	35.6	30.1	41.1	15
Fibres	666.1	423.2	909.0	36	8,205.9	5,213.2	11,198.7	36	719.8	457.3	982.3	36
Shells	281.8	179.0	384.6	36	4,382.0	2,783.8	5,980.1	36	379.1	240.9	517.4	36
Kernel	230.0	29.5	430.5	87	4,266.8	547.8	7,985.8	87				
Biogas	45.3	28.8	62.0	37	1,042.3	663.3	1,424.9	37	227.1	144.5	310.5	37
Crude Palm Oil	987.9	835.2	1,140.6	15	38,121.6	34,040.0	42,203.1	11	3,006.9	2,542.1	3,471.6	15
Biodiesel	***Quantity (kg)***			**Co-efficient Variations *(%)***	***Energy Eq. (MJ $_{eq.}$)***			**Co-efficient Variations *(%)***	***Carbon Eq. (kg $CO_{2\,eq.}$)***			**Co-efficient Variations *(%)***
	Median	**Min**	**Max**		**Median**	**Min**	**Max**		**Median**	**Min**	**Max**	
Crude Palm Oil	987.9	835.2	1,140.6	15	38,121.6	34,040.0	42,203.1	11	3,006.9	2,542.1	3,471.6	15
Water	250.9	145.3	356.4	42								
Electricity (kWh)	156.2	5.0	307.4	97	554.3	1.8	1,106.7	100	97.8	0.3	195.3	100
Methanol	136.8	93.2	180.5	32	4,423.9	2,062.3	6,785.6	53	156.8	73.6	240.0	53
Sodium Hydroxide	6.0	2.0	10.0	67	157.4	52.6	262.3	67	4.7	1.6	7.9	67
Wastewater	250.9	145.3	356.4	42								
Glycerol	110.0	110.0	110.0	0	6,204.0	6,204.0	6,204.0	0	157.3	157.3	157.3	0
Biodiesel	1,000.0	1,000.0	1,000.0	0	39,600.0	39,600.0	39,600.0	0	2,823.0	2,823.0	2,823.0	0

Figures 3.5, 3.8 and 3.9 are graphical presentations of the data from *Table 3.4*, using a spider diagram to demonstrate the variation of data across the 11 chosen studies. In terms of the parameters (Palm Oil Plantation, Crude Oil Production, and Transesterification), they all include each stage's respective inputs and outputs, including products passed onto the next stage. The data sets are not entirely consistent and there are fluctuations across the chart due to missing data.

In *Figure 3.5*, within the Palm Oil Plantation 'Agriculture' stage, the FFB make up a majority of the quantity for most studies, Pleanjai *et al.* [84] forming an extreme. This is because of the amount of fertiliser that Pleanjai *et al.* [84] assume to be required, in which the other studies differ in analysis. They also claim to high quantities in the Crude Oil Production 'Processing' parameter, which can also be seen in their follow-up review [83], but this is predominantly because they have more complete data sets than the other studies. These have some values missing, for instance Achten *et al.* [330], who provided little processing data.

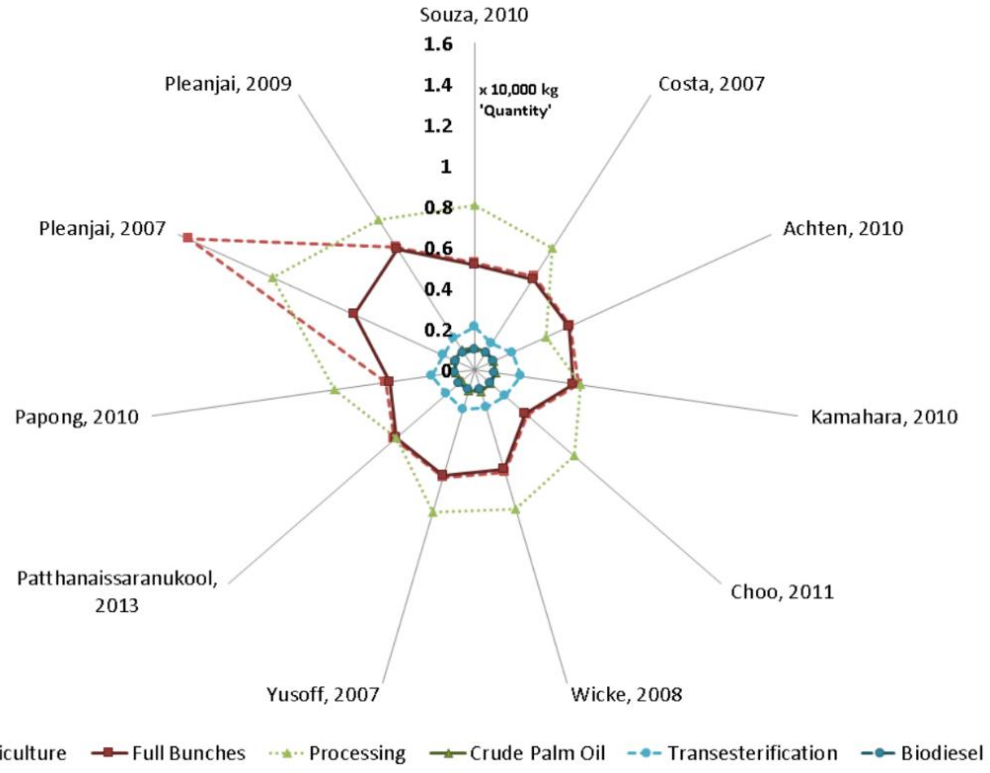

Figure 3.5: Input and output quantity data variations for 1,000 kg POBD FU for 11 LCA study references.
Data sources: [82-86, 327, 329, 330, 333, 335, 337]

The reason the key indicators of the POBD system (FFB/CPO/POBD) have received so much attention is because of the extent of the missing or unknown data for energy and carbon equivalence values. The other parameters have been added to demonstrate how much incomplete data sets can obscure the results, although most fields have been filled with similarly sourced data. The common known values for the FFB and CPO parameters are that

for every 1,000 kg CPO produced approx. 5,000 kg FFB are required [326]. *Figures 3.6* and *3.7* highlight the extent of study variations based on these findings.

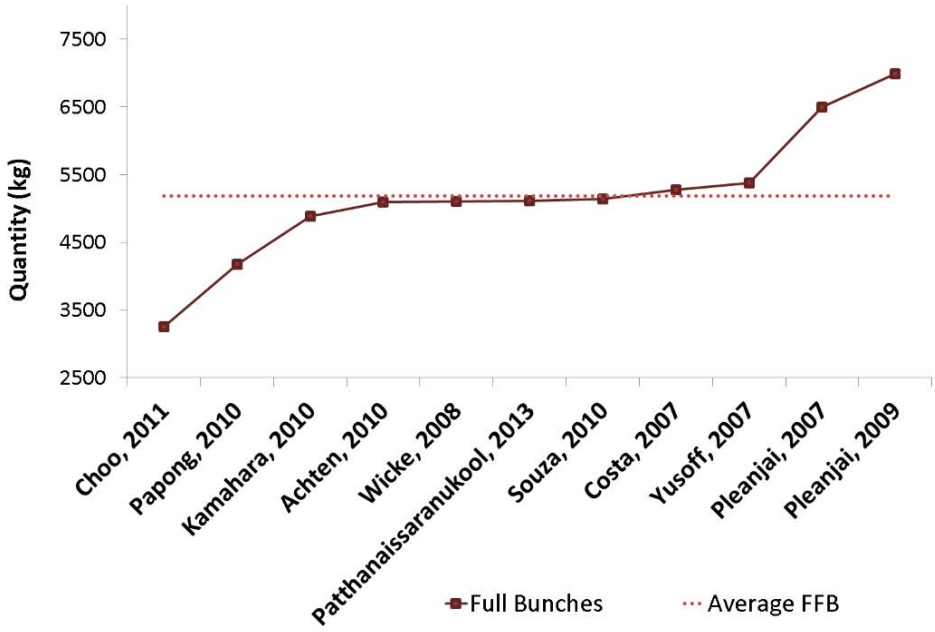

Figure 3.6: Quantity of FFB necessary for producing 1,000 kg POBD vs the average from 11 LCA study references.

Data Sources: [82-86, 327, 329, 330, 333, 335, 337]

The horizontal dotted lines in *Figures 3.6* and *3.7* show the averages of the FFB and CPO production data sets, respectively. The solid lines demonstrate which studies are either close to or far from average. Both Pleanjai *et al*. [83, 84] studies are consistently above average, due to having more complete data sets. Conversely, Papong *et al*. [337] is under average for both. Reasons for these variations also consist of geographic locations, plantation sizes, technology efficiency and age, and production methods.

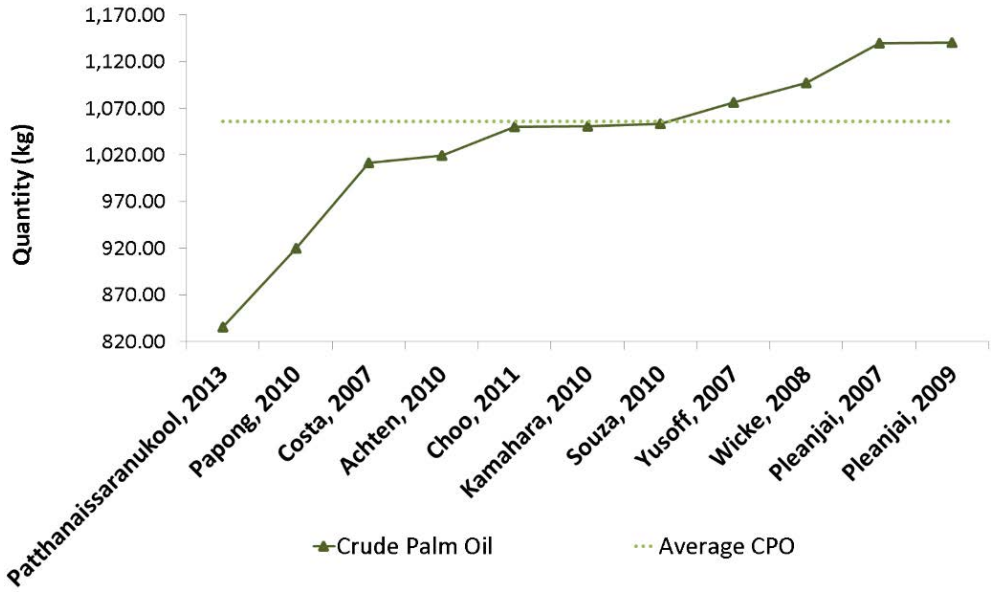

Figure 3.7: Quantity of CPO necessary for producing 1,000 kg POBD vs the average from 11 LCA study references.

Data sources: [82-86, 327, 329, 330, 333, 335, 337]

Souza *et al*. [329] and Kamahara *et al*. [85] are the two most consistent studies for both FFB and CPO processing, in accordance with average production. The low CPO value of Patthanaissaranukool *et al*. [82] in *Figure 3.7* is one of the studies to have more consistent FFB production, whereas Choo *et al*. [86] has less consistent FFB data than CPO with the averages. If methodological deviations are cancelled out, possible parameter variations could be influenced by ageing technology, plantation harvest technique variations, or lower quality of harvests due to climate impacts.

b) Energy Equivalence Data

The energy equivalence data (*Figure 3.8*) was produced using reported energy equivalence values for LCI data (*Table 3.4*). The FU was set at the energy equivalence of 1,000 kg POBD for all 11 studies and equalled 39,600 $MJ_{eq.}$/1,000 kg POBD. The CPO values were slightly more consistent for energy equivalence data compared to quantity data, fluctuating closely around 38,121 $MJ_{eq.}$/1,000 kg POBD ±10%. The FFB data set had higher variation between studies, at 78,040 $MJ_{eq.}$/1,000 kg POBD ±33%.

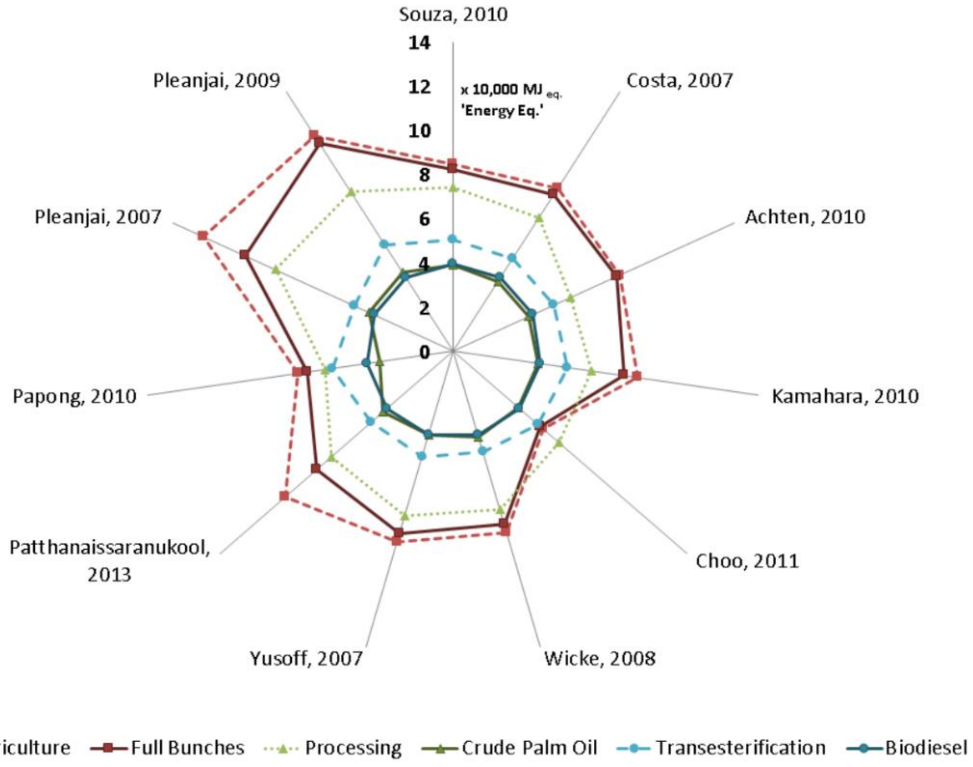

Figure 3.8: Energy equivalence data variations for 1,000 kg POBD FU for 11 LCA study references.
Data sources: [82-86, 327, 329, 330, 333, 335, 337]

Both Pleanjai *et al.* [83, 84] studies have the highest energy values again, but as before, this is because of their more complete data sets and higher energy data for the key indicators (FFB/CPO/POBD). The data from the other studies is reasonably consistent, demonstrated by the homogenous patterns, Achten *et al.* [330] being the exception due to their lack of processing data.

It should be recognised that the angularity of *Figure 3.5* is significantly higher than in *Figure 3.8*, demonstrating that energy data is in better agreement across the studies than quantity data. However, as the energy equivalence data is directly derived from the quantity data, it is interesting how *Figure 3.8* is more homogenous than *Figure 3.5,* as it would be expected that similar data patterns would be produced. This illustrates the importance of evaluating more than one aspect to receive a more complete assessment of inter-study heterogeneity.

c) Carbon Equivalence Data

The carbon equivalence data (*Figure 3.9)* was the most incomplete data set, having most fields missing due to lack of published data and/or unknown values. Like the data for energy equivalence, this data was produced by using carbon equivalence or 'kg $CO_{2\ eq.}$' values from other literature for the relevant items (also shown in *Table 3.4*). POBD data was set at the same carbon equivalence value across all 11 studies: 2,823 kg $CO_{2\ eq.}$/1,000 kg POBD. This was calculated using the amount of combustible organic carbon content within the biodiesel methyl ester that could produce carbon dioxide when used in an internal combustion engine.

The carbon equivalence for CPO was calculated to be around 3,006 kg $CO_{2\ eq.}$/1,000 kg POBD ±15%, which was based on a POBD organic carbon content of 83%. The FFB carbon values were calculated the same as CPO, based on 31% organic carbon content and quantity. There were some significant variations for 'Processing', due to the lack of data set completeness, as before, much unlike the more downstream data sets that show greater consistency between studies. As Achten *et al.* [330] is the only study for Cameroon, and no comparable geographical site data available to fill in the gaps, its incompleteness demonstrates how the reliability of such sources can be easily corrupted.

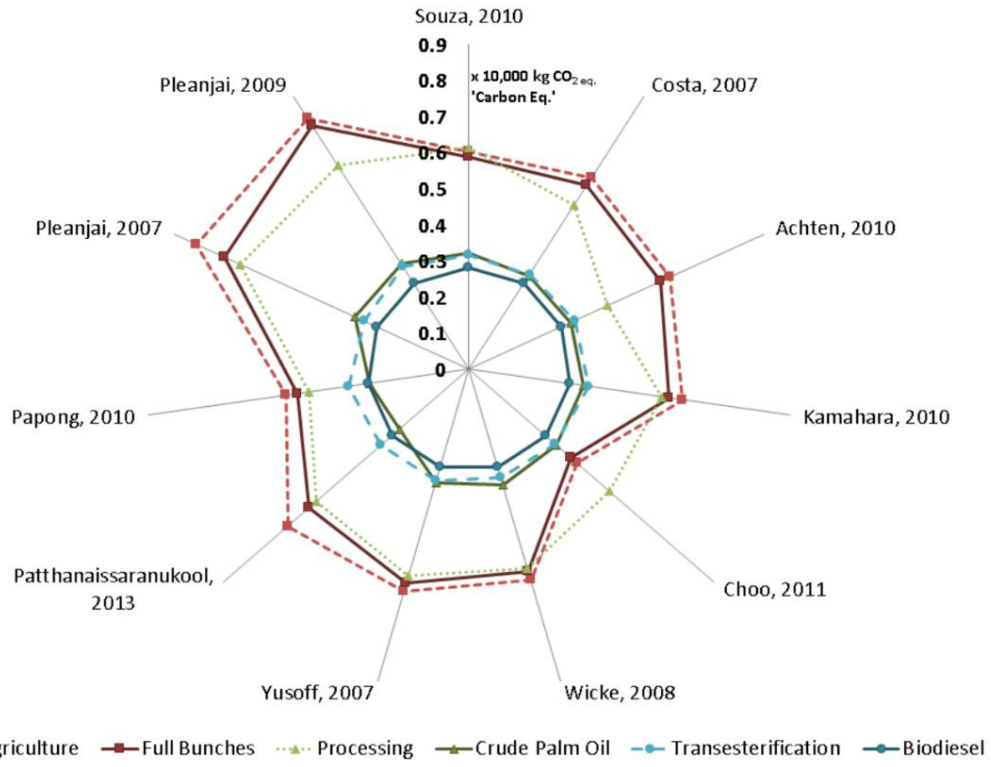

Figure 3.9: Carbon equivalence data variations for 1,000 kg POBD FU for 11 LCA study references

Data sources: [82-86, 327, 329, 330, 333, 335, 337]

3.5.6. Meta-Analysis Results

The meta-analysis results showed that the level of comprehensiveness affects the comparability of studies in terms of transparency, accuracy, and reliability. Although all the data sets provided reasonably consistent stage three POBD data, the input data for stage one FFB and stage two CPO data were more heterogeneous, due probably to specific difficulties with individual items in gathering data and/or variations of the life cycle methodologies applied. For instance, the amount of CPO produced depends on the different contributions of mass for the FFBs as they go through the Crude Oil Production 'Processing' stage. This is demonstrated in *Figure 3.10;* each bar represents what is present inside each total output of FFB/FU.

There are eight complementary and complete data sets [82-86, 327, 329, 335], as they have all five parameters: EFB, Fibres, Shells, Kernel, and CPO. However, Achten *et al.* [330] was the most incomplete data set, with only CPO, Fibres and Shells data. This is a direct reflection

on the individual studies' methodological choices and without other Cameroon studies in this analysis there was no additional data to fill in data set gaps with. Papong *et al.* [337] was also incomplete, as kernel data was not present in their study, due to individual methodical choices. The most interesting study in *Figure 3.10* was Wicke *et al.* [333], as despite having average results for FFB and CPO processing in *Figures 3.6* and *3.7*, it had the greatest level of discrepancy for FFB mass contribution. Others may have considered excluding studies like these from their assessment, but that also removes the greater question of why there are this many inconsistencies in FFB products that should grow the same way and produce the same component proportions. For instance, why are there more kernel shells in Wicke *et al*. [333] study compared to all the others? Are the shells thicker? or kernels smaller? These are all unobtainable answers, but without including data such as these their original questions would never have been asked.

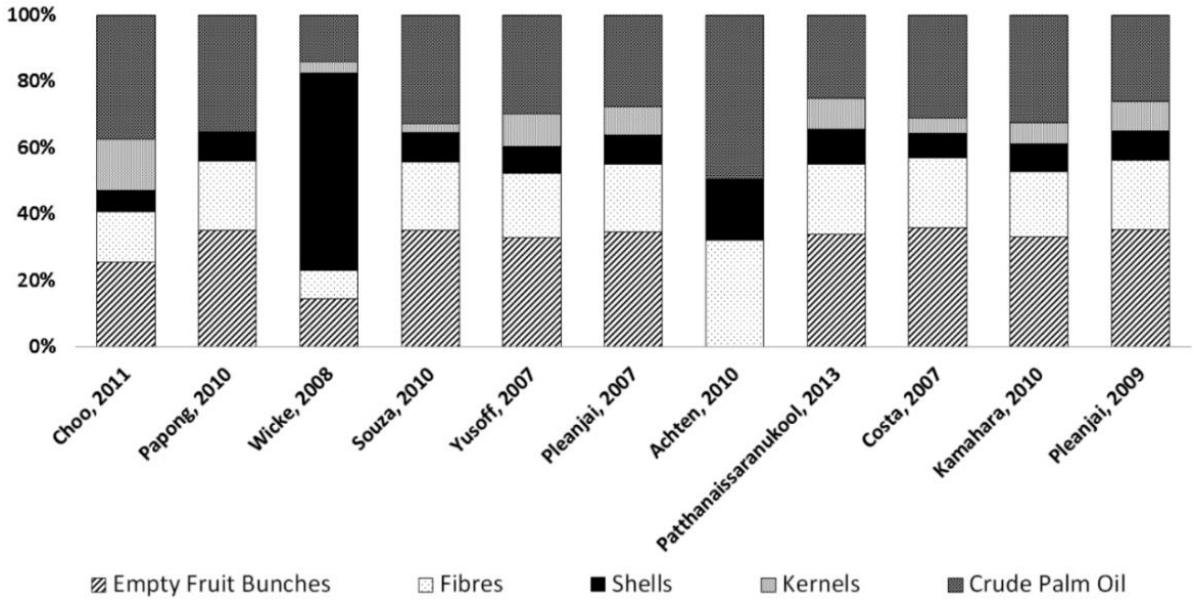

Figure 3.10: Percentage mass contribution of FFB components for 11 LCA study references

Data sources: [82-86, 327, 329, 330, 333, 335, 337]

This diversity in data completeness for all stages of LCA demonstrates how important it is to ensure that all data fields, if not as many as possible, are fully represented in an LCA, so that

inconsistencies and data discrepancies are avoided. When using existing studies, care should be taken to evaluate the depth of data shown and how transparent the studies are.

The final area of analysis is on the data sets themselves. Variance analysis was performed to demonstrate the extent of data variation for each parameter (*Figure 3.11*). Parameters showing thinner black bars demonstrate data with no or little variation between studies, such as the amount of CPO needed. The zero error for the POBD was because this was a pre-determined fixed point for this analysis. The vertical lines protruding from the boxes represent the range between the highest and lowest values. The boxes themselves represent the ranges between the median and average values, pale boxes have averages below the median, dark boxes have averages above the median. A set of consistent data sets would have most of the parameters having little difference between average and median and low variance, if any.

Figure 3.11, part A shows variances between the quantity data for FFB having the largest variation, followed by boiler water in the central processing stage. The extent of the FFB data variance emphasises the wide range between data sets. Whereas in *Figure 3.11, part B,* the greatest variance is still the FFB, with nitrogen fertiliser also having ranges in energy equivalence data; this trend in FFB is also true in *Figure 3.11, part C*.

Some fields are missing across all the data sets for energy and carbon equivalence values, which do not have bars or values. As previously stated, these omissions could be due to the limitations of the study data sets in terms of completeness, but they could also be due to differences in geography and/or plantation/industrial process variations. Improvements for this data analysis would be to fill in the missing slots with data acquired from generic process information or derived from similar geographical sources, as previously stated, so that all parameters are populated.

Regarding practical assessment of parameter variations in this research field, most of the impact comes from techno-economic reports, which cover a variety of inputs and outputs – especially costs. These reports emphasise the importance of including parameter uncertainties, as not doing so can produce misleading results [340]. They also find that engineering inevitabilities (such as reduced production efficiencies, and underdeveloped energy networks and transportation infrastructure), which are common across developing countries, cause technological uncertainties. These can result in higher prices for biodiesel production and feedstock and instability in the market [341, 342]. Crude palm oil is the most influencing parameter in biodiesel production [340, 343], so when newer papers do not include CPO in their data sets, it is also increasing the uncertainty in the LCA field. Much like the variations between the LCIs investigated in this chapter, by not discussing them and producing an LCI from only two or three papers, or even missing out parameters altogether, increases the potential of misrepresentation.

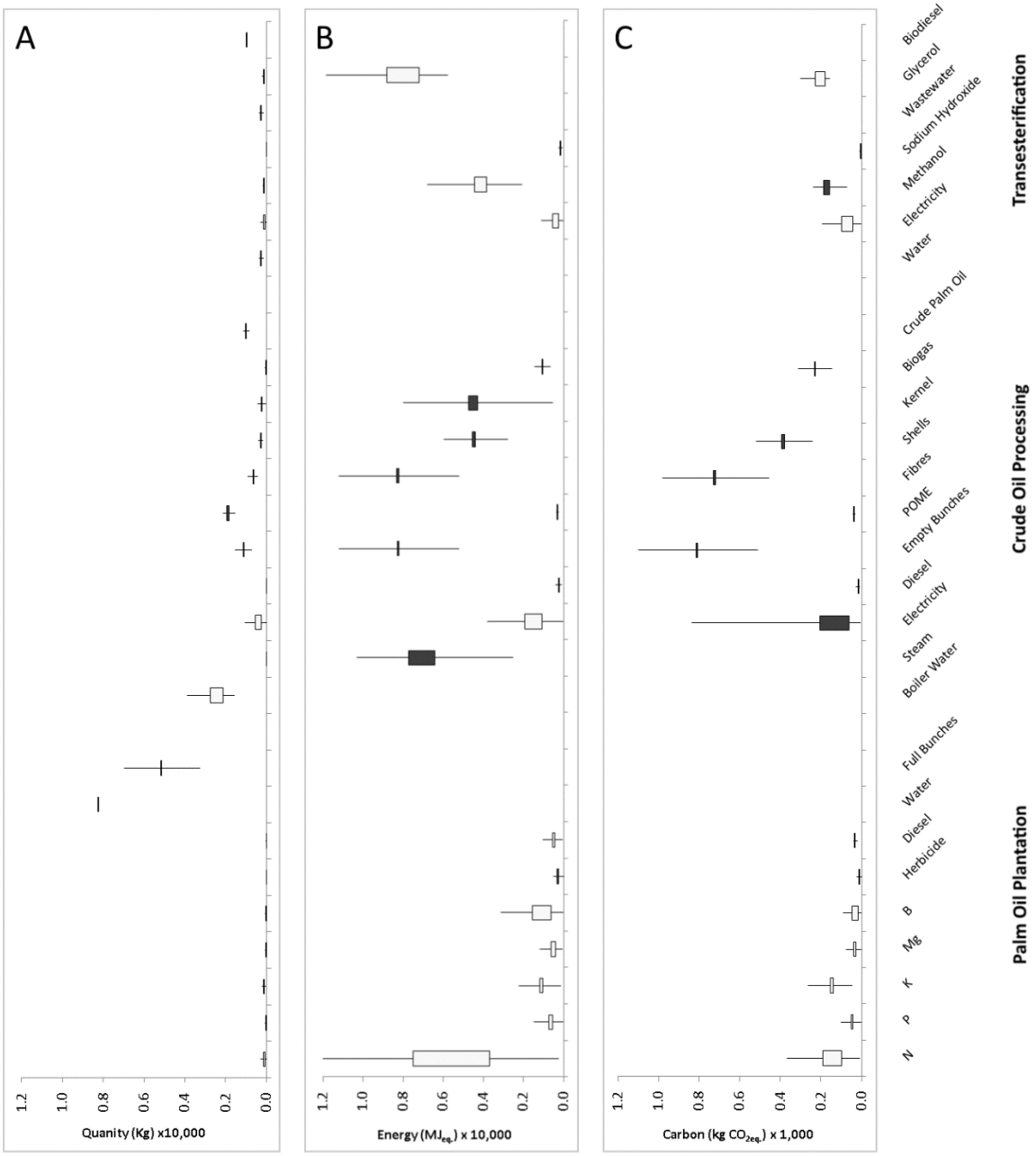

Figure 3.11: Palm oil plantation, crude oil production, and transesterification data set parameters with co-efficient variations for 1,000 kg POBD FU for 11 LCA studies for: A – Quantity, B – Energy equivalence, and C – Carbon equivalence.

Data sources: [82-86, 327, 329, 330, 333, 335, 337]

3.5.7. Discussion

Many studies of similar geographic origin had similar data, which in turn varied in comparison to other geographies, as demonstrated in *Figures 3.5, 3.8,* and *3.9*. Therefore, special attention must be given that studies of similar geographical origin are used in comparisons. In contrast, a major source of variation between studies arose from methodological differences. The specificity of data collection and system boundaries was by

far the largest contributor, as studies with higher percentages of original data, e.g. both Pleanjai *et al*. [83, 84] studies, were found to be more accurate than those with high levels of synthesised data e.g. Achten *et al*. [330]. The degree of homogenisation also impacted on the accuracy of data, as studies with POBD FUs were not influenced as much as those with CPO FUs.

In summary, the flexibility of the ISO 14040 and 14044 standards in offering a practitioner a choice in setting the study parameters inevitably means that the individual configurations of different studies on similar or the same products – in this case POBD – will necessarily lead to some diversity in results. It is therefore mandatory to evaluate carefully the relevance of a given study to the LCA question(s) being asked and, as has been done here, ideally to aggregate data and results from several relevant studies (including additional bridging of any data gaps *etc*. where needed) to obtain an appropriate and generic perspective on the LCA evidence.

This study provides support to the increased interest in biomass research on fuels for the transport sector. There is a current lack of reliable LCA research in this area. The study was intended to contribute to evaluating the variations occurring across selected POBD LCA studies, to help others find more reliable studies. One example being that studies with either lesser or greater data set completeness, amongst other factors, can greatly influence the overall results.

3.6. Conclusions

This study presents a novel, 11 study comparison and data set formation for product, energy, and carbon equivalent values for the 'Well to Tank' assessment of POBD.

As part of the in-depth exploration of variation between different LCAs of palm oil biodiesel (POBD), this study has assembled a comparison inventory of quantities, energy, and carbon

equivalence analyses to produce POBD and its co-products. The process of aligning LCA data from several publications and other sources revealed substantial heterogeneity in the reporting of system boundaries, methodological approaches, and basic data between studies. A FU of production of 1,000 kg POBD was utilised to scale the reported inputs, outputs, and environmental impacts to derive representative and well characterised generic values and data ranges.

Biodiesel is an important step towards the market introduction of renewable transport fuels and it is essential that its environmental performance is reliably evaluated through internationally recognised methods such as LCA. The presented study found that variations between seemingly similar LCA studies are caused by inconsistencies in data collection and methodological choices, such as system boundaries, geography, and other details such as parameter choices. Through the use of careful processes for data and results evaluation, filtering, and assimilation, these can be accommodated in compiling an appropriate generic LCI assessment for POBD.

The core key findings from this research was presented through the provision of an alternative perspective not typically seen in within this field. The use of data units in LCI and LCA research was thought to have been a personal choice; whichever units fits the model best, so to speak. However, in reality, each of these units can provide their own individual influence, which can result in further inconsistences between studies. Therefore, the choices made through the methodological and data set production phases can have a greater impact in the wider field than was originally believed.

CHAPTER 4

This chapter is based on a publication by S.A. Archer, with the support and editorial feedback from R. Steinberger-Wilckens (University of Birmingham), which was published under open access (CC-BY 4.0)

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CHAPTER 4. SYSTEMATIC ANALYSIS OF HYDROGEN PATHWAYS FROM BIOMASS

4.1. The Potential for Biomass

This chapter focuses on various (waste) biomass streams and investigates the sustainable potential of these biomass pathways for production of fuel gases for fuel cells [344]. It assesses production efficiencies, upgrading/reforming, and added value products. Agriculture can provide sources for biogas production from energy crops or wastes, using anaerobic digesters [345]. This technology can be used to change current aerobic digestion of wastes onsite (typically compost piles, which produce ammonia and carbon dioxide, or landfills) to anaerobic processes, which produce and capture biogas.

Biomass can extend to include waste streams, such as municipal solid wastes, animal wastes, and food processing wastes, or aquatic plants, including algae [70]. Biomass residues and wastes can be used as feedstock for the production of sustainable, 'carbon-neutral' hydrogen from various biopolymers like carbohydrates and lignin that are produced during the growth of biomass [70, 346]. Waste biomass streams should be prioritised over using resources with existing markets. Using unutilised waste biomass decreases demands and competition for existing products, namely food, by providing new resources that can provide the same end product – gaseous or liquid energy vectors.

In the following, the term 'biomass' will therefore be limited to biological wastes, embracing virtually zero costs for the feedstock, or even earning a premium by disposing of the waste agricultural slurries and waste residues, like straw, stover, and digestate, and recycled waste streams, such as forestry trimmings. Using biomass conversion pathways that yield hydrogen-rich gases like biogas and syngas (*Table 4.1*) can provide alternatives for fossil

natural gas and can produce higher useable gas yields than direct hydrogen extraction for example from biohydrogen producing algae.

Table 4.1: Molar compositions of Biogas and Syngas
Adapted from: [230, 233, 347-349]

Molar Composition of Biogas				Molar Composition of Syngas			
Methane	CH_4	→	~85%	Hydrogen	H_2	→	~45%
Carbon Dioxide	CO_2	→	~13%	Carbon Monoxide	CO	→	~42
Nitrogen	N_2	→	~1%	Carbon Dioxide	CO_2	→	~8 %
Hydrogen Sulphide	H_2S	→	~0.5%	Methane	CH_4	→	~5%
Silicon Dioxide	SiO_2	→	~0.5%	Sulphur Dioxide	SO_2	→	~0.5%

As biogas and syngas are rich in hydrogen content, they can be used directly (after removal of impurities) in boilers, engines, and fuel cells [e.g. combined heat and power (CHP) plants] or reformed to pure hydrogen, for use in fuel cell vehicles. Thus, a shift from fossil fuel natural gas and crude oil to hydrogen-rich gases from biological and waste sources could reduce both the demand for primary fossil resources and the amount of waste sent to landfill [225], as well as avoiding fossil carbon dioxide release to the atmosphere.

4.1.1. Systematic Analysis Methodology

Seven methods of biomass conversion to hydrogen-rich fuel gases were investigated via systematic literature review (*Chapter 2*) of the core processes, their variations (light/dark or aerobic/anaerobic), and feedstocks (summarised in *Section 4.2*). Each pathway has been summarised with inputs, outputs, and additional processes for fuel upgrading/cleaning, consolidated, and linked to its final product (biogas/hydrogen/syngas). Common biomass feedstocks for each pathway were identified from literature. Efficiency data was explored and compared against two reference cases, namely use of natural gas or fossil hydrogen in a fuel cell (*Section 4.3*).

4.2. Biomass Paths to Fuel Gases

The growing interest in biomass use for energy supply has resulted in the development of many conversion techniques to produce biofuels: biological (fermentation, anaerobic digestion, and metabolic processing), thermochemical (gasification and supercritical water gasification (SCWG) for gas production, and pyrolysis and subsequent liquefaction for liquid fuels), and extraction of carbohydrates, lipids, and hydrocarbons, *e.g.* for alcohol and biodiesel production. *Figure 2.1* (*Chapter 2, page 26*) offers a comprehensive overview of the different pathways of turning biomass into an energy vector compatible with today's energy markets. Many of these pathways result in gaseous fuels that are immediately useful for operating high temperature fuel cells (including any mixtures containing hydrogen, carbon monoxide, and methane, for example) or even supply hydrogen at various purity levels. These biomass pathways and hydrogen extraction methods have been discussed in detail in [130], and have been summarised across a multitude of papers [70, 77-81, 130, 172, 350-357]. Specific reference to hydrogen and fuel gases for use in fuel cells was made in [356, 358, 359], also covering direct hydrogen production from algae [360]. Life Cycle Analysis of some of these production methods was covered in [361, 362].

Figure 2.1 demonstrates the complexity of biomass conversion, as there are many cross-overs between different pathways, for instance when unutilised by-products from one pathway can be utilised as another's input (i.e. anaerobic digestion digestate or algal biomass for liquefaction). The flow chart is structured as per the legend, with the start of the pathways in the numbered boxes. Products throughout each stage are highlighted with thicker outlined boxes. Regarding the variety of uses these products have, the primary and secondary processes demonstrate the natural flow of where the product is currently used (primary – solid lines), and if there is an upgrading/clean-up process (secondary – dotted lines) to produce a more refined product. The alternative flows (dashed lines) show

substitute applications, for instance if the bio-char produced in pyrolysis/liquefaction is not sold for revenue but is combusted (as substitute for coal) for electricity/heat generation.

There are five principal pathways that produce a variety of hydrogen-rich gases from biomass. Biomass sources high in carbohydrates and proteins, such as agricultural crop wastes (*i.e.* straw and stover [363]), and waste fats and vegetable oils from food preparation [364] can be utilised by biological conversion techniques, (1) anaerobic digestion, (2) metabolic processing, and (3) fermentation, and to produce biogas, methane, and hydrogen. Alternatively, thermochemical conversion techniques, (4) gasification and (5) SCWG, utilise predominately lignocellulosic biomass (ranging from forestry residues to perennial grasses [365]) to produce syngas. Increasingly, the feedstocks are sourced from waste streams that do not impact, or are complementary to, food markets. Use of waste vegetable oils is increasing in raw materials markets, such as those for liquid fuels.

In addition, there are four pathways producing liquid fuels: Pyrolysis, Liquefaction, and Extraction of lipids/hydrocarbons and carbohydrates (which are un-numbered in *Figure 2.1*), with diesel, gasoline/petroleum, kerosene, methanol, and ethanol as an output. Liquefaction can be utilised by both thermochemical and biological conversion feedstocks, as long as the biomass has a high moisture content – such as agricultural wastes and slurries. The resulting bio-oil can be refined into liquid fuels. The final pathway is Combustion/Co-firing (also un-numbered), which is currently the most common method of biomass utilisation [366-372]. One of the unmentioned by-products of pyrolysis is syngas, which is not further mentioned here since it is generally used within the plant for producing process heat [373, 374]. These five pathways will not be assessed as part of this chapter and are only mentioned here for completeness, due to the focus being on gaseous fuels for fuel cells alone.

4.2.1. Pathway Summary

The different pathways and their fuel gas outputs are summarised in *Table 4.2*. Natural gas and hydrogen produced by steam reforming of natural gas are included as reference cases, although only the gas energy value is considered as there is no biomass input. The efficiencies of these pathways will be further evaluated in the following sections.

Algal metabolic processing (Pathway 2) and fermentation (Pathway 3) both produce hydrogen directly, whilst anaerobic digestion (Pathway 1), gasification (Pathway 4) and SCWG (Pathway 5) have the potential to produce pure hydrogen with clean-up and reforming processes. Examples of these additional processes for reforming and/or purification include steam methane reforming, water-gas shift reaction, and gas separation (pressure swing adsorption (PSA) or an activated carbon filter).

Alternatively, there is also dry reforming, which is a catalytic reaction where methane is reformed with carbon dioxide to produce syngas [375], much like that produced by gasification and SCWG. Carbon monoxide/carbon dioxide can then be removed from the syngas via PSA to leave only hydrogen or the syngas to be processed directly in a high temperature fuel cell [376].

Liquid fuel pathways (pyrolysis and liquefaction) have been excluded due to this chapter focusing on gaseous products. Although one of the by-products of pyrolysis is syngas, it is predominately used as onsite energy during the pyrolysis process and enhancing the drying of inputted biomass (for inclusive systems) [373, 374]. Therefore, including it was seen to be interfering with existing markets, not utilising wastes.

The nature of hydrogen production from metabolic processing should also be considered. As this process is photobiological, there is no initial input of raw biomass, only algae and what it needs to grow and produce the hydrogen alongside growth. Therefore, there are no feedstock energy values for the live algae.

Table 4.2: Biological and thermochemical pathway summaries and chemical reaction equations for conversion stages

Background sources: Anaerobic Digestion – [131, 134-136, 147, 377, 378], Metabolic Processing – [164-169, 174, 182, 379], Fermentation – [81, 171, 176, 190-193, 202, 203], Gasification – [216, 217, 219, 225, 380], SCWG – [230, 231, 380-382], RC Natural Gas – [383], RC Hydrogen – [354, 384-386].

	Pathway	Inputs	Feedstock Energy Value		Outputs	By-Products	Process Stage	Process Chemical Reaction Equations	Refs
			as received (kWh_{eq}/kg)	*dry and ash free* (kWh_{eq}/kg)					
1	**Anaerobic Digestion**	Plant Biomass Animal Slurry Biowastes	4.16	5.2	Biogas[a].	Digestate Sludge.	Hydrolysis Acidogensis Acetogensis Methanogensis *Overall Reaction*	(1) $C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + H_2$ (2) $C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$ (3) $C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O$ (4) $C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$ (5) $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (6) $CH_3COOH \rightarrow CH_4 + CO_2$ (7) $C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2$	[157] [157] [157] [157, 160] [157, 160] [157, 160] [389]
2	**Metabolic Processing**	Carbon Dioxide Water Nutrients	n/a[b]	n/a[b]	Hydrogen.	Oxygen. Recycled Carbon Dioxide Bioreactor Sludge.	Direct Photobiolysis Indirect Photobiolysis ATP Phase *Overall Reaction*	(8) Photons + $2H_2O \rightarrow 2H_2 + O_2$ (9) $2H^+ + 2e^- \rightarrow H_2 + e$ (10) Photons + $6H_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2$ (11) $C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2$ (12) Photons + $2CH_3COOH + 4H_2O \rightarrow 12H_2 + 4CO_2$ (13) $2H^+ + 2e^- + 4ATP \rightarrow H_2 + 4ADP + 4Pi$ (inorganic phosphate) (14) Photons + $12H_2O + \rightarrow 12\ H_2 + 6CO_2$	[81, 91, 187, 188, 194, 390] [191] [81, 91, 187, 188, 194, 199] [91, 188] [91, 188] [188, 191] [188]
3a	**Dark Fermentation**	Biowastes (& Anaerobic Digestate / Bioreactor Sludge)	3.05	5.28	Hydrogen	Acetic Acid. Recycled Carbon Dioxide	Hetrotrophic bacteria	(15) $C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$	[188]
3b	**Light Fermentation**	Biowastes (& Anaerobic Digestate / Bioreactor Sludge)	3.05	5.28	Hydrogen	Recycled Carbon Dioxide	Phototrophic bacteria Two stage fermentation	(16) Photons + $4H_2O + 2CH_3COOH \rightarrow 4CO_2 + 6H_2$ (17) $C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2$	[188, 197, 210, 215 [188, 210]
4	**Gasification**	Dry Biomass	4.36	5.78	Syngas[c]	Slag/Ash	Dry gasification Water-gas shift reaction	(18) Heat + $2C_6H_{10}O_5 + 4H_2O \rightarrow 10H_2 + 6CO + 4CO_2 + 2CH_4$ (19) $6CO + 6H_2O \rightarrow 6CO_2 + 6H_2$	[231, 232] [91]
5	**Supercritical Water Gasification**	Wet Biomass Water	4.36	1.97	Syngas[c]		Wet gasification Water-gas shift reaction	(20) Heat + $2C_6H_{10}O_5 + 5H_2O \rightarrow 13H_2 + 7CO + 4CO_2 + CH_4$ (21) $7CO + 7H_2O \rightarrow 7CO_2 + 7H_2$	[250, 386] [91]
RCa	***Reference Case NG***	*Grid Natural Gas*	*n/a*[f]	*n/a*[f]	*De-sulphured Natural Gas*	*Contaminant Gases (Sulphur)*	*Desulphuration*	*(22) $[CH_4 + C_2H_6 + N_2 + CO_2 + SO_2] + C \rightarrow [CH_4 + C_2H_6 + N_2 + CO_2] + [SO_2 + C]$*	*[384, 394]*
RCb	***Reference Case H2***	*De-sulphured Natural Gas*	*n/a*[f]	*n/a*[f]	*(Fossil) Hydrogen*	*Carbon Dioxide*	*Steam reforming*	*(23) $CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$*	*[80]*

Assumed chemical compositions, equations, and feedstock energy values from literature and Phyllis2 [247, 250, 360-362, 391-393]:

a Biogas composition (~85% CH_4, ~13% CO_2, ~1% N_2, ~0.5% H_2S, ~0.5% SiO_2)

b Metabolic processing has no raw biomass input (photobiological process)

c Syngas composition (~45% CO_2, ~42% CO, ~8% CH_4, ~5% H_2, ~0.5% SO_2)

d SCWG utilises wet biomass, therefore no dry value is provided.

e Natural Gas composition (~95% CH_4, ~2.5% C_2H_6, ~1.5% N_2, <1% CO_2, <0.5% SO_2)

f Natural Gas has no feedstock as there is no biomass input.

4.2.2. Fuels for Fuel Cells

This study compares the different biomass conversion systems and the fuels they produce and combines them with different fuel cell applications. The fuel cells operating at the lowest and highest temperatures (Polymer Electrolyte Fuel Cell (PEFC) and Solid Oxide Fuel Cell (SOFC)) are the chosen technologies for assessment. This is not just due to their operating conditions, but also because they are the most commonly deployed fuel cells and demonstrate both the narrowest and widest use of gaseous fuels. Other fuel cell types include Alkaline (AFC), Phosphoric Acid (PAFC), Molten Carbonate (MCFC), and Direct Methanol/Ethanol (DMFC & DEFC) Fuel Cells, as explored in *Chapter 2*.

4.3. Pathway Comparison

The five pathways analysed in *Table 4.2* convert biomass using different methods to yield a variety of fuel gas products. Most of these fuels can be utilised in the different fuel cell technologies explored, some of which have internal reforming, such as SOFCs [358], but gases may require cleaning up to prevent, for example, sulphur poisoning [358]. This is due to catalysts, such as platinum or nickel, being very sensitive to impurities including sulphur, particulate matter, corrosive components such as chlorine or fluorine, and siloxanes (oxidises into silicon dioxide), which will compromise the performance and efficiency of the fuel cell.

In *Table 4.3*, chosen pathway outputs, fuel gas clean-up/reforming processes, fuel gas lower heating values (LHVs), and the potential fuel cell applications have been summarised.

Table 4.3: Biomass conversion pathways, produced fuel gases, and potential fuel cell applications.

Separation and purification sources: [144, 154, 155, 158, 236, 393]

	Pathway	Outputs	Possible Gas Clean-up / Reforming Process(es)	Fuel Gas	Fuel LHV *(kWh_e/kg)*	Fuel Cell Applications
1	**Anaerobic Digestion**	Biogas.	H_2S, & SiO_2 removal via pressure swing adsorption (PSA).	Biogas.	10.00	SOFC, MCFC.
			CO_2, N_2, H_2S, & SiO_2 removal via PSA.	Biomethane.	13.89	SOFC, MCFC.
			Steam reformed biomethane/water-gas shift (WGS) and purification.	Hydrogen (BM).	33.34	SOFC, (MCFC*), PAFC, AFC, PEFC.
2	**Metabolic Processing**	Hydrogen.	Separation from O_2 and recycled CO_2 via PSA.	Hydrogen.	33.34	SOFC, (MCFC*), PAFC, AFC, PEFC.
3a	**Dark Fermentation**	Hydrogen.	Separation from O_2 and recycled CO_2 via PSA.	Hydrogen.	33.34	SOFC, (MCFC*), PAFC, AFC, PEFC.
3b	**Light Fermentation**	Hydrogen.	Separation from O_2 and recycled CO_2 via PSA.	Hydrogen.	33.34	SOFC, (MCFC*), PAFC, AFC, PEFC.
4	**Gasification**	Syngas.	Removal of particulates and corrosive components (SO_2).	Syngas.	3.61	SOFC, MCFC.
			WGS and separation.	Hydrogen (SG).	33.34	SOFC, (MCFC*), PAFC, AFC, PEFC.
5	**Supercritical Water Gasification**	Syngas.	Removal of particulates and corrosive components (SO_2).	Syngas.	3.61	SOFC, MCFC.
			WGS and separation.	Hydrogen (SG).	33.34	SOFC, (MCFC*), PAFC, AFC, PEFC.
RCa	***Reference Case Natural Gas (NG)***	*De-sulphured Natural Gas.*	*Absorption separation process to remove sulphur.*	*De-sulphured Natural Gas.*	*13.89*	*SOFC, MCFC.*
RCb	***Reference Case H_2***	*(Fossil) Hydrogen.*	*Steam reformed natural gas/WGS and purification.*	*(Fossil) Hydrogen.*	*33.34*	*SOFC, (MCFC*), PAFC, AFC, PEFC.*

Gas compositions as in Table 5.1; (*) allowing for additional carbon dioxide feed to the cathode.

Fuels with high energy content, such as hydrogen, are predominately the result of additional processing. However, it is also directly produced in two biological processes, metabolic conversion, and light/dark fermentation. Nevertheless, both of these pathways initially have low efficiencies, due to the (photo)biological limitations of the micro-organisms involved [161]. The pathway efficiencies for gas production, clean-up/reforming processes, and use of fuel gases have been calculated below. *Figure 4.3* demonstrates how the data set was calculated, including research from first principals, and how the whole system works together, with products undergoing four stages of conversion: *Stage 1* – raw biomass to useable 'chemical' feedstock, *Stage 2* – feedstock to raw gas, *Stage 3* - raw gas to fuel gas, and *Stage 4* – fuel gas to electrical output.

These stages were calculated in reverse order, owing to the choice of 1 MWh of electrical fuel cell output as the functional unit , similar to the data set produced for *Chapter 3*. The amount of biomass feedstock and fuel gas was required at each stage was calculated starting from *Stage 4* and working backwards, based on available data and background research *[Equations 4.24 to 4.30]*.

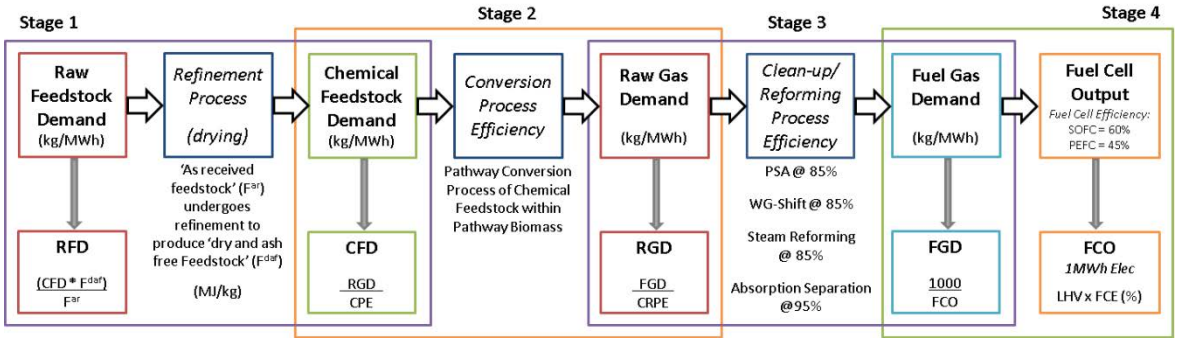


Figure 4.1: Raw biomass feedstock to fuel gas process chain

For *Stage 4,* the specific 'fuel cell output' (FCO) required to produce a functional unit of 1 MWh electrical output was calculated as shown in *Equation 4.24*, using the fuel gas LHV

and 'fuel cell efficiency' (FCE). The FCO was then used to determine the 'fuel gas demand' (FGD) for this 1 MWh system, using *Equation 4.25* to convert from kWh to MWh.

$$FCO\ (kWh_e/kg) = LHV * FCE \qquad [4.24]$$

$$FGD\ (kg) = 1000 / FCO \qquad [4.25]$$

The 'raw gas demand' (RGD) was calculated for *Stage 3* to determine how many kg of unprocessed raw gas were produced per MWh of feedstock *[Equation 4.26]*. This used the fuel gas demand (FGD) and (if any) 'clean-up/reforming process efficiencies' (CRPE) for refined fuels. For CRPE of PEFC fuel gases, only the purification via PSA process applies, as SOFCs conversely have (internal) reforming processes already included in the fuel cell efficiency itself. If there is more than one clean-up/reforming step, *Equation 4.27* is implemented as part of *Equation 4.26,* with the mol $^{wt}\%$ being applied when separating specific gas from a mixed fuel, i.e. $^{wt.}\%$ of methane content within biogas for extraction and clean-up.

$$RGD\ (kg/MWh) = FGD\ (\ /\ CRPE\ )\ \textit{if applicable} \qquad [4.26]$$

$$CRPE\ (\%) = Eff._1 * Eff._2\ * mol\ ^{wt.}\% \qquad [4.27]$$

To make this assessment complete, the total feedstock involved in the pathway was also required, so that lower efficiency pathways were better represented. The 'chemical feedstock demand' (CFD) was calculated for *Stage 2* (*Equation 4.28*), using the RGD divided by the pathway's 'conversion process efficiency' (CPE). This corresponds to the chemical conversion reactions (glucose/cellulose *etc.*) within the raw waste biomass, which varies with each pathway.

$$CFD\ (kg/MWh) = RGD / CPE \qquad [4.28]$$

The overall equation for calculating FGD from CFD is shown in *Equation 4.29*:

$$FGD\ (kg/MWh) = CFD * CPE * CRPE \qquad [4.29]$$

Once the CFD has been calculated, the calculation for *Stage 1* can be made to determine the amount of raw feedstock demand (RFD) required. It is assumed that any raw feedstock received will go through refinement processing first (drying, sorting, homogenising *etc.*); only the useful components in wet and dry condition (as received feedstock, F^{ar}) will be referred to. For further calculation of conversion stages, the dry and ash free feedstock (F^{daf}) was considered as the pure chemical fuel component stripped of any inorganic matter. As a technical process, this will not be completely accurate since an 'ash removal' will normally take place within the conversion process, e.g. as the ash from combustion or sand deposits in fermentation. Nevertheless, in the physio-chemical processes involved, only the chemical energy content (enthalpy, HV) of the feedstock will be converted, thus effectively referring to the convertible substance fraction alone (i.e. in F^{ar}). Therefore, this concept in back-tracing the total amount of feedstock required was used, since online biomass databases, such as Phyllis2 [390], provide LHV data for the two categories F^{daf} and F^{ar}. By using these two values, the CFD can be converted to RFD, as in *Equation 4.30,* by transforming between units of kg and MJ.

$$(CFD\ (kg/MWh) * F^{daf}\ (MJ/kg)) / F^{ar}\ (MJ/kg) = RFD\ (kg/MWh) \qquad [4.30]$$

It is with this RFD unit that original feedstock that is required per MWh of electrical output from the produced gaseous fuel can determined, thus offering an assessment of the overall efficiency of the process chain and the effort in supplying the feedstock.

4.3.1. Fuel Cell Fuels Analysis

All biological pathways discussed above can provide fuels for the fuel cell technologies discussed. This is because metabolic processing and fermentation directly produce hydrogen, with the advantage of being able to use waste feedstocks. Conversely, thermochemical pathways predominately produce fuels for high temperature fuel cells, at

a high efficiency, with reforming options for producing hydrogen for the low temperature fuel cells. The most commonly used fuel cells at the time are SOFC for high temperature and PEFC for low temperature, and so these were used for further analysis, displayed in *Table 4.4.* The pathway efficiencies shown are the initial conversion efficiencies for the chemical compositions of the biomass feedstocks found across literature. These efficiencies, as explained above, apply purely for the convertible part of the biomass.

Anaerobic digestion and gasification efficiencies are assumed at 75% [394-396]; for SCWG the value is taken as 70% [397, 398]. The clean-up and reforming efficiencies are representative for the convertible gases (biomethane/natural gas) with 85% efficiency [386, 399]. This is also true for upgrading carbon monoxide, from syngas, into hydrogen using a water-gas shift reaction (WGS), with 85% efficiency [207]. Research has been conducted with catalyst membranes, potentially increasing WGS efficiency up to 95% [400, 401]. 1 kg of Biomethane is produced from ~1.4 kg biogas (87%). Hydrogen produced from biomethane and syngas requires an additional purification process with 85% efficiency before entering the (low temperature) fuel cell.

The biological hydrogen pathways are slightly different, as their efficiencies are determined by the biological limitations of the organisms driving the reaction. The algae producing hydrogen via metabolic processing have a maximum production efficiency of 10% [161, 181]. Dark and light fermentation bacteria have a low biological conversion (15% and 10%, respectively [172]) but a high hydrolysis conversion efficiency of 50% and 80% [193]. This results in pathway efficiencies of 9% and 6%. The clean-up efficiencies for these pathways are 85%, reflecting an 80 to 90% PSA efficiency [63, 402].

For the natural gas and fossil hydrogen reference cases, the initial process efficiencies for extraction of raw natural gas from a reserve (gas well) is estimated to be up to 80% [403].

However, advancing techniques of extracting additional raw natural gas have been explored, and therefore an estimated efficiency of 85% will be used for the reference case systems, but it is recognised that raw natural gas is not comparable to extraction of gases from biomass. For the production of de-sulphured natural gas, an activated charcoal filter is used at a 95% efficiency [404]. This natural gas can also produce (fossil) hydrogen via steam reforming at 85% efficiency.

A first inspection of *Table 4.4* shows that SOFCs are more efficient in converting biomass-derived fuels than PEFC, due to their higher performance and greater variation of fuels. Of these 19 pathways (twelve SOFC vs. seven PEFC), *Table 4.4* initially found anaerobic digestion biogas and gasification syngas to be the most efficient pathways at 75%.

Table 4.4: Full biomass and reference case pathways, their fuels, and efficiencies for SOFC and PEFC

Data modified from: [63, 132, 161, 172, 181, 193, 352, 390, 391, 394-398, 400-402, 405-413]

	Pathway	Process Efficiency	Gas Clean-up / Reforming Efficiency	Fuel Gas	Fuel LHV *(kWh_e/kg)*	Fuel Cell Efficiency	Fuel Gas Demand (kg/MWh)	Feedstock Energy Value: *Chemical Feedstock (kg/MWh)*	Feedstock Energy Value: *Post-refinement - dry and ash free (kWh_e/kg)*	Feedstock Energy Value: *Biomass - as received (kWh_e/kg)*	Raw Feedstock Demand (kg/MWh)
1a	**Anaerobic Digestion**	75%	*95%*	Biogas.	10.00	SOFC (60%$^{eff.}$)	166.65	*236.18*	*n/a*	*4.16*	*236.18*
1b			85%	Biomethane.	13.89	SOFC (60%$^{eff.}$)	119.99	*221.44*	*n/a*	*4.16*	*221.44*
1c			85%	Hydrogen (BM).	33.34	SOFC (60%$^{eff.}$)	49.99	*217.05*	*n/a*	*4.16*	*217.05*
			85%	Hydrogen (BM).	33.34	PEFC (45%$^{eff.}$)	66.66	*289.45*	*n/a*	*4.16*	*289.45*
2	**Metabolic Processing**	10%	85%	Hydrogen.	33.34	SOFC (60%$^{eff.}$)	49.99	*n/a*	*n/a*	*n/a*	*858.62*
			85%	Hydrogen.	33.34	PEFC (45%$^{eff.}$)	66.66	*n/a*	*n/a*	*n/a*	*1,144.94*
3a	**Dark Fermentation**	9%	85%	Hydrogen.	33.34	SOFC (60%$^{eff.}$)	49.99	*653.46*	*5.29*	*3.05*	*1,131.52*
			85%	Hydrogen.	33.34	PEFC (45%$^{eff.}$)	66.66	*871.39*	*5.29*	*3.05*	*1,508.88*
3b	**Light Fermentation**	6%	85%	Hydrogen.	33.34	SOFC (60%$^{eff.}$)	49.99	*1,069.30*	*5.29*	*3.05*	*1,851.58*
			85%	Hydrogen.	33.34	PEFC (45%$^{eff.}$)	66.66	*1,425.91*	*5.29*	*3.05*	*2,469.07*
4a	**Gasification**	75%	*95%*	Syngas.	3.61	SOFC (60%$^{eff.}$)	461.50	*650.98*	*5.78*	*4.36*	*863.82*
4b			85%	Hydrogen (SG).	33.34	SOFC (60%$^{eff.}$)	49.99	*922.56*	*5.78*	*4.36*	*1,224.20*
			85%	Hydrogen (SG).	33.34	PEFC (45%$^{eff.}$)	66.66	*1,224.10*	*5.78*	*4.36*	*1,624.34*
5a	**SCWG**	70%	*95%*	Syngas.	3.61	SOFC (60%$^{eff.}$)	461.50	*697.48*	*n/a*	*4.36*	*697.48*
5b			85%	Hydrogen (SG).	33.34	SOFC (60%$^{eff.}$)	49.99	*988.50*	*n/a*	*4.36*	*988.50*
			85%	Hydrogen (SG).	33.34	PEFC (45%$^{eff.}$)	66.66	*1,318.00*	*n/a*	*4.36*	*1,318.00*
RCa	***Reference Case NG***	*85%**	*95%*	*De-sulphured Natural*	*13.89*	*SOFC (60%$^{eff.}$)*	*157.98*	*207.87*	*n/a*	*n/a*	*207.87*
RCb	***Reference Case H2***	*85%**	*85%*	*(Fossil) Hydrogen*	*33.34*	*SOFC (60%$^{eff.}$)*	*49.99*	*182.07*	*n/a*	*n/a*	*182.07*
			85%	*(Fossil) Hydrogen*	*33.34*	*PEFC (45%$^{eff.}$)*	*66.66*	*242.80*	*n/a*	*n/a*	*242.80*

* Sour Natural Gas, extracted from gas well (extraction efficiency assumed)

The fuel cell output represents the amount of electrical output (kWh_e) possible from 1 kg of fuel gas. The fuel gas demand denotes the quantity of fuel gas required to deliver the 1 MWh fuel cell electrical output functional unit. *Equation 4.25* demonstrates how the data is converted from kWh to MWh. Ideally, the lower the quantity of fuel gas required to achieve the 1 MWh functional unit, the more sustainable its performance. Seven of the twelve SOFC fuels achieved the lowest quantities, at 50 kg/MWh, due to the high electrical efficiency and the high gravimetric energy density of hydrogen fuel. All seven PEFC fuels used 66 kg/MWh due to the lower FUE. Three of the SOFC fuels had fuel gas demands below 175 kg/MWh; the other two were up to 500kg. Unfortunately, the amount of fuel gas alone does not allow any estimates of sustainability of the specific pathway. The key factors here are the electrical efficiency of the fuel cell and the high gravimetric energy density of hydrogen fuel.

However, some pathways produce higher gas yields per kg of feedstock than others, so to allow for this, the feedstock demand for each pathway's fuel gas demand was calculated. These were established based on the reaction equations explored in *Section 4.2*, as well as literature data. This was predominately due to the varieties of different reactor types, capacities, outputs, and feedstock LHVs.

Of the biological pathways, algae perform biological metabolic processing, which directly uses photons from light to produce energy for breaking down water. The solar conversion efficiency is very low due to their biological limitations (<10%) [181]. Light fermentation bacteria also have these constraints. Some bacteria that are used in dark fermentation cannot produce hydrogen directly due to thermodynamic constraints [172]; some bacteria cope with this by producing methane first, which they can then break down into carbon

dioxide and hydrogen. This inhibition decreases their biological performance down to <15% conversion efficiency [172, 191].

In addition, both fermentation pathways have a wide range of substrate hydrolysis efficiencies *i.e.* consumption of feedstock (30 to 40% up to 80 to 95%) depending on the composition of the feedstock [81, 193]. Algal bioreactor sludge was utilised as a feedstock in this analysis, which has an estimated 65% (±15%) substrate hydrolysis efficiency for dark fermentation and 55% (±10%) for light fermentation [193]. When simplified to include both biological limitations and substrate efficiencies, the pathway efficiencies for dark and light fermentation are estimated to be 9% and 6%, respectively. Due to the feedstock demand having the highest level of influence, the above findings have the potential to reorder the performance ranking across the 19 pathways.

4.4. Key Findings

The fuel gas pathways and fuel cell combinations were highlighted based on best performances across four parameters: fuel cell output, fuel gas demands, raw gas demands, and raw feedstock demands. These affect each pathway's performance for producing a 1 MWh of fuel cell electrical output and have been ranked in order of lowest to highest feedstock use (*Table 4.5*). This ranking aims to reflect the efficiency of the process chain to produce a given amount of electricity by inspecting the amount of feedstock necessary. This amount not only indicates the quantity of feedstock, but also hints at transport energy requirements. In interpreting this table, though, care must be given to the quality of the feedstock. A lower quality feedstock (e.g. sewage sludge) may imply higher mass but might be preferable to higher value feedstock (e.g. waste fats) that could be put to alternative uses. This aspect, though, has not been fully investigated in this chapter. Nevertheless, *Table 4.5* gives first indications of feedstock quality.

Ref.	Fuel Gas	Fuel Cell Type	Fuel Gas LHV (kWh/kg)	Fuel Gas Demand (kg/MWh)	Raw Feedstock Demand (kg/MWh)	Biomass to Fuel Gas (kg/kg)	Rank	Raw Feedstock Input	Raw Feedstock LHV (kWh/kg)	Equivalent Combustion Quantity (kg/MWh) Dry Biomass at 70%$^{eff.}$
1a	Biogas	SOFC (60%$^{eff.}$)	10.00	166.65	236.18	1.42	3	Biowastes[1]	*As Received* : 3.33	*n/a*
1b	Biomethane	SOFC (60%$^{eff.}$)	13.89	119.99	221.44	1.85	2	Biowastes[1]	*Dry**: 4.72	302.66
1c	Hydrogen (BM)	SOFC (60%$^{eff.}$)	33.34	49.99	217.05	4.34	1	Biowastes[1]		
1c	Hydrogen (BM)	PEFC (45%$^{eff.}$)	33.34	66.66	289.45	4.34	4	Biowastes[1]		
2	Hydrogen	SOFC (60%$^{eff.}$)	33.34	49.99	858.62	17.18	6	Algae[2]	*As Received* : 4.86	*n/a*
2	Hydrogen	PEFC (45%$^{eff.}$)	33.34	66.66	1,144.94	17.18	10	Algae[2]	*Dry**: 23.52	60.74
3a	Hydrogen	SOFC (60%$^{eff.}$)	33.34	49.99	1,131.52	22.63	9	Biowastes[1]	*As Received* : 3.05	*n/a*
3a	Hydrogen	PEFC (45%$^{eff.}$)	33.34	66.66	1,508.88	22.63	13	Biowastes[1]	*Dry**: 5.29	270.05
3b	Hydrogen	SOFC (60%$^{eff.}$)	33.34	49.99	1,851.58	37.04	15	Biowastes[1]	*As Received* : 3.05	*n/a*
3b	Hydrogen	PEFC (45%$^{eff.}$)	33.34	66.66	2,469.07	37.04	16	Biowastes[1]	*Dry**: 5.29	270.05
4a	Syngas	SOFC (60%$^{eff.}$)	3.61	461.50	863.82	1.87	7	Woody biomass[3]	*As Received* : 4.36	327.65
4b	Hydrogen (SG)	SOFC (60%$^{eff.}$)	33.34	49.99	1,224.20	24.49	11	Woody biomass[3]	*Dry***: 5.78	247.16
4b	Hydrogen (SG)	PEFC (45%$^{eff.}$)	33.34	66.66	1,624.34	24.37	14	Woody biomass[3]		
5a	Syngas	SOFC (60%$^{eff.}$)	3.61	461.50	697.48	1.51	5	Woody biomass[3]	*As Received* : 4.36	327.65
5b	Hydrogen (SG)	SOFC (60%$^{eff.}$)	33.34	49.99	988.50	19.77	8	Woody biomass[3]	*Dry***: 5.78	247.16
5b	Hydrogen (SG)	PEFC (45%$^{eff.}$)	33.34	66.66	1,318.00	19.77	12	Woody biomass[3]		
RCa	*De-sulphured Natural Gas*	*SOFC (60%$^{eff.}$)*	*13.89*	*157.98*	*n/a*	*n/a*	*17*	*Sour Natural Gas*[4]	*13.10^*	*179.99*
RCb	*(Fossil) Hydrogen*	*SOFC (60%$^{eff.}$)*	*33.34*	*49.99*	*n/a*	*n/a*	*18*	*Sour Natural Gas*[4]	*33.34^*	*74.99*
RCb	*(Fossil) Hydrogen*	PEFC (45%$^{eff.}$)	*33.34*	*66.66*	*n/a*	*n/a*	*19*	*Sour Natural Gas*[4]	*33.34^*	*74.99*

[1] Agricultural slurries (up to 90%^{MC}) and waste crop residues (up to 65%^{MC})

[2] Algal mass requirements (up to 90%^{MC})

[3] Sustainable forestry residues, logging rejects, infested wood etc (up to 30%^{MC})

** Drying biomass requires a lot of process energy (**low intensity drying)*

^ Natural Gas Combustion Engine use (~40%$^{eff.}$)

[4] Sour Natural Gas, extracted from reserve, therefore no feedstock demand.

Reference guide:

1a Anaerobic Digestion, Biogas
1b Anaerobic Digestion, Biomethane from Biogas
1c Anaerobic Digestion, Hydrogen from Biomethane
2 Metabolic Processing, Hydrogen
3a Dark Fermentation, Hydrogen
3b Light Fermentation, Hydrogen
4a Gasification, Syngas
4b Gasification, Hydrogen from Syngas
5a Supercritical Water Gasification, Syngas
5b Supercritical Water Gasification, Hydrogen from Syngas
RCa Reference Case, Natural Gas
RCb Reference Case, Hydrogen from Natural Gas

Table 4.5: Pathway summary table ranked in feedstock demand performance

Out of the biological pathways, anaerobic digestion hydrogen from biomethane, biogas, and biomethane had the lowest feedstock demands, fuel gas demands, and highest fuel cell output, followed by biohydrogen between syngas from SCWG and gasification. It is understood that using natural gas reference cases do not utilise biomass, and therefore do not have raw feedstock demand results to allow for fully comparable values. However, by comparing the performance of existing pathways to that of alternative pathways, it is possible to scale the process chains against the reference cases, if not only by the raw gas demand. All three top ranking pathways refer to SOFC systems. Both fermentation pathways showed the most promising performance, regarding high fuel cell output and low fuel gas demand, but have the highest feedstock demands due to the low process efficiencies, with metabolic processing ranking in the mid-tier.

Overall, this chapter has found the following:

i. In this analysis, methane rich fuels have greater performance, due to the high gravimetric energy density and fewer processing stages than necessary for hydrogen production, when used in SOFC.
ii. Syngas and metabolic processing methods predominately have only slightly greater biomass feedstock demands. Light and dark fermentation have the highest, but can be combined for higher hydrogen yields, as well as metabolic processing, which could potentially reduce their high feedstock demand in future assessments.
iii. Anaerobic digestion and SCWG have the highest process efficiencies, followed by gasification. They have low to mid-range fuel gas and feedstock demands due to their high input/high yield processes.

iv. Hydrogen from fermentation and hydrogen from SCWG and gasification syngas have the highest fuel gas demand and mid-range feedstock demands due to a low heating value.

v. The natural gas and fossil hydrogen reference cases are only presented for comparison and to demonstrate how competitive other pathways can be. Since they do not rely on any 'feedstock', a final comparison can only be based on environmental impact (*Chapter 5*). Nevertheless, it can be stated that the conversion efficiency (gas cleaning and reforming to hydrogen) do not differ from the biomass based pathways and the fossil carbon of the fuel will lead to considerable net carbon dioxide emissions. Biomass based fuels have low inherent net carbon emissions due to the processing energy required, since all biogenic carbon has been previously sequestrated from the atmosphere. This aspect is taken care of in the efficiency calculations.

vi. SOFC technologies outperformed PEFCs, with their internal reforming capabilities allowing for a higher variation of fuel gases.

In addition to this assessment, it was found that each pathway feedstock determines the yield of fuel gases, and so high stack fuel demand may not be an issue if the biomass feedstock demand is low. Examples of this are the hydrogen pathways. They have low conversion process efficiency and fuel cell outputs, but moderate fuel gas and feedstock demands, due to the high gravimetric energy density of hydrogen, which increases the pathway's initial performance. This factor demonstrates the importance of looking at multiple perspectives in thoroughly assessing both the pathways and the technologies involved.

The performance of fermentation and metabolic processing pathways are a common theme across literature. Their low process efficiencies are due to the biological limitations, within the organisms themselves, for sunlight conversion. However, due to the purity of the hydrogen produced and high hydrogen yields per dry cellular mass, the low efficiency of the fermentation processes does not out-weigh their potential. To improve metabolic processing, genetically engineered algae and bacteria would help the technology to become commercially viable. This would result in higher yields of hydrogen with a higher efficiency rate. These modifications at a cellular level could increase growth, speed up the uptake of glucose, sucrose *etc.,* and promote the continuous hydrogen production without inhibition [175, 414]. Therefore, increasing the biological efficiency would significantly improve these biological pathways across all areas, as well as decrease the size (and therefore cost) of the bioreactors required to produce the same, if not higher, hydrogen yields.

4.5. Conclusions

Promising pathways for using biomass sources to derive gases for fuel cell applications were: anaerobic digestion, SCWG, and metabolic processing. These pathways can utilise agro-waste residues, slurries, lignocellulosic wastes, and wastewater from agricultural sectors to effectively produce useful gaseous fuels. Conversely, the raw gas demand results of the two reference cases are not specifically superior to the biomass pathways, showing that these are competitive systems. As natural gas and fossil hydrogen are based on fossil fuel sources, they do not constitute sustainable pathways. An additional finding was that the potential for fuel gas uses can vary due to the variation of biomass feedstock and fuel gas yields produced from these conversion pathways, including sources for both SOFCs and PEFCs.

Key findings of this chapter include the insight that even pathways with low efficiency and high fuel gas demands have the potential to be more sustainable. This is due to higher yielding biomass feedstock, compared to pathways with higher efficiency, low fuel gas demands, and higher feedstock demands. SOFCs proved to be a more favourable technology than PEFCs, due to their wide range of fuel choices and higher efficiency.

CHAPTER 5

This chapter is based on an original research article by S.A. Archer, with the supervision of R. Steinberger-Wilckens and Dr Andrew Ingram (University of Birmingham), and has been submitted for journal publication review.

CHAPTER 5. COMPARATIVE LIFE CYCLE ANALYSIS OF BIOMASS DERIVED FUELS FOR FUEL CELLS

5.1. The Demands for Cleaner Gas

There are a multitude of possible fuels that can be utilised for fuel cells, many of which can come from biological feedstocks and biowastes (*Chapters 2 and 4*). Biomass derived fuels have the advantage that any carbon emitted in the form of carbon dioxide has initially been short-term sequestrated from the atmosphere during growth. If this biogenic carbon dioxide is then captured, it is accredited negative emissions, as carbon dioxide has then been removed from the biological cycle. Conversely, fossil resources have long term temporal impacts as they have been removed from the carbon cycle for too long to still have a neutral effect. Therefore, fuel cells with net carbon emissions only result from using fossil resources. In comparing fossil and biomass sourced fuels, though, a full appraisal including other environmental impacts has to be performed using Life Cycle Analysis (LCA).

The LCA presented here is broken down into four stages: Goal and Scope (*Section 5.2*), Inventory Analysis (*Section 5.3*), Impact Assessment (*Section 5.4*), and Interpretation of the results (*Section 5.5*), which involves substance and sub-process contribution analyses [279]. In order to comply with ISO 14044 LCA standards, the impact categories that will be used as part of this assessment are also stated, and their environmental impact defined [279].

5.2. Goal and Scope

This study has been carried out as part of an investigation into available fuel gases for use in fuel cells, in an effort to show the potential of reducing dependency on fossil fuels. The intended audiences are researchers and industry within the field of hydrogen production, fuel cells, and alternative biofuels.

The intent of this study was to assess sustainable hydrogen and gaseous fuel sources from the biomass conversion pathways identified in [68] for use in fuel cells. An assessment of both SOFCs and PEFCs was undertaken in *Chapter 4* to evaluate their fuel supply chains and fuel use performance. This was achieved through the calculating of biomass to gas data, using literature data, chemistry, and molar properties from first principals (Table 5.1), which will be used as in this study's LCA inventory data set. This research identified how much raw biomass was required to make the amount of raw gas necessary for a 1 MWh equivalent amount of fuel gas for use in each fuel cell type. Each technological and processing stage had their efficiencies considered, as well as losses in mass. The resulting findings were ordered from lowest to highest raw biomass feedstock demand (*Table 5.1*). It was found that SOFCs not only have greater performance efficiency than PEFCs (~60% vs ~45%, respectively [251, 254]), but also a significant variety of useable fuels; unlike PEFCs that typically only use hydrogen.

Three fossil fuel reference cases have also been assessed: natural gas (for SOFC) and hydrogen produced by steam reforming (for both SOFC and PEFC systems), without the burden of fuel production, for comparability. Hydrogen is presently mainly produced from natural gas via a steam reformation process, which makes current hydrogen supply dependant on the fossil fuel market. Natural gas can also be used directly in SOFCs once sulphur has been removed.

The functional unit used throughout this assessment is (A) Whole System Analysis: 1 MWh of electrical output of the fuel cell, which utilises (B) Fuel Gas Analysis: the equivalent quantity of fuel required to produce (A); and (C) Raw Gas Analysis: the required input of raw gas required to produce (B). Functional units (B) and (C) provide additional comparative quantities that are equivalent to (A), which contain deeper, detailed results for the sub-

processes that make up the whole system. Each of these units were produced in *Chapter 4's* pathway assessment.

Table 5.1: Biomass derived fuels for fuel cells and reference cases – master data set

	Pathway	Fuel Gas	Fuel LHV		Process Efficiency	Gas Clean-up / Reforming Efficiency (%)	Fuel Cell Type	Fuel Cell Efficiency (%)	Fuel Cell Output (kWh/kg)	Fuel Gas Demand (kg/MWh)	Raw Gas Demand (kg/MWh)	Feedstock Energy Value			Raw Feedstock Demand (kg/MWh)	Stack CO_2 Emissions (kg/MWh) *CO_2 neutral	Stack Water Output (kg/MWh)
			kWh/kg	*MJ/kg*								*Chemical Feedstock Demand (kg/MWh)*	*Post-refinement - dry and ash free (MJ/kg)*	*Biomass - as received (MJ/kg)*			
1a	Anaerobic Digestion	Biogas	10.00	19	75%	*95%*	SOFC	60%	6.00	166.65	177.13	*236.18*	*n/a*	*14.98*	236.18	236.00*	202.61
1b		Biomethane	13.89	50		85%	SOFC	60%	8.33	119.99	166.08	*221.44*	*n/a*	*14.98*	221.44	197.99*	323.97
1c		Hydrogen (BM)	33.34	120		85%	SOFC	60%	20.00	49.99	162.79	*217.05*	*n/a*	*14.98*	217.05	0	269.95
		Hydrogen (BM)	33.34	120		85%	PEFC	45%	15.00	66.66	217.09	*289.45*	*n/a*	*14.98*	289.45	0	269.97
2	Metabolic Processing	Biohydrogen	33.34	120	10%	85%	SOFC	60%	20.00	49.99	58.81	*n/a*	*n/a*	*n/a*	858.62	0	269.95
		Biohydrogen	33.34	120		85%	PEFC	45%	15.00	66.66	78.42	*n/a*	*n/a*	*n/a*	1144.94	0	269.97
3a	Dark Fermentation	Hydrogen	33.34	120	9%	85%	SOFC	60%	20.00	49.99	58.81	*653.46*	*19.03*	*10.99*	1,131.52	0	269.95
		Hydrogen	33.34	120		85%	PEFC	45%	15.00	66.66	78.43	*871.39*	*19.03*	*10.99*	1,508.88	0	269.97
3b	Light Fermentation	Hydrogen	33.34	120	6%	85%	SOFC	60%	20.00	49.99	58.81	*1,069.30*	*19.03*	*10.99*	1,851.58	0	269.95
		Hydrogen	33.34	120		85%	PEFC	45%	15.00	66.66	78.43	*1,425.91*	*19.03*	*10.99*	2,469.07	0	269.97
4a	Gasification	Syngas	3.61	13	75%	*95%*	SOFC	60%	2.17	461.50	488.23	*650.98*	*20.82*	*15.69*	863.82	713.83*	294.30
4b		Hydrogen (SG)	33.34	120		85%	SOFC	60%	20.00	49.99	691.92	*922.56*	*20.82*	*15.69*	1,224.20	0	269.95
		Hydrogen (SG)	33.34	120		85%	PEFC	45%	15.00	66.66	918.08	*1,224.10*	*20.82*	*15.69*	1,624.34	0	269.97
5a	SCWG	Syngas	3.61	13	70%	*95%*	SOFC	60%	2.17	461.50	488.23	*697.48*	*n/a*	*15.69*	697.48	713.83*	294.30
5b		Hydrogen (SG)	33.34	120		85%	SOFC	60%	20.00	49.99	691.95	*988.50*	*n/a*	*15.69*	988.50	0	269.95
		Hydrogen (SG)	33.34	120		85%	PEFC	45%	15.00	66.66	922.60	*1,318.00*	*n/a*	*15.69*	1,318.00	0	269.97
RCa	*Reference Case NG*	*De-sulphured Natural Gas*	*10.55*	*43*	*80%*	*95%*	*SOFC*	*60%*	*6.33*	*157.98*	*165.96*	*207.45*	*n/a*	*n/a*	*207.45*	*256.17*	*418.01*
RCb	*Reference Case H2*	*(Fossil) Hydrogen*	*33.34*	*120*	*80%*	*85%*	*SOFC*	*60%*	*20.00*	*49.99*	*145.36*	*181.71*	*n/a*	*n/a*	*181.71*	*0*	269.95
		(Fossil) Hydrogen	*33.34*	*120*		*85%*	*PEFC*	*45%*	*15.00*	*66.66*	*194.24*	*242.80*	*n/a*	*n/a*	*242.80*	*0*	269.97

The primary and secondary information required to synthesise data for (B) and (C) were compiled using the same methodologies, in addition to substance production and infrastructure data from the EcoInvent 3.2 database. The results for individual systems generated using the life cycle impact assessment method, CML-IA baseline, with identical data entry types (Allocated, Default) and reporting categories for the generation of characterised data results, as per ISO 14025 [299], which were produced from SimaPro LCA Software and the built-in EcoInvent 3.2 database. Alternatively, the data can be normalised into a single unit, which can be expressed as either: 'EU domestic impact per person per year' or 'Impacts from an EU geographic per year' [301, 302] through the application of EU developed 'normalisation factors' (*Section 5.4, Table 5.3*). This produces a dimensionless value, across all impact categories, allowing them to be compared directly alongside small quantity, high potency impacts [415].

The aim of this study was to investigate and assess the environmental impact of fuels derived from biomass (both their production and use in fuel cells), how they compare amongst each other (and to the respective fossil fuel reference cases) from an environmental perspective, and what the demand for biomass/biowaste feedstock is. The systematic analysis previously conducted in *Chapter 4* involved an assessment of each pathway's efficiency for producing and cleaning up raw gases from waste biomass, including the conversion from mass to gas.

This analysis found that the anaerobic digestion biogas (1a-SOFC), biomethane (1b-SOFC), and algal metabolic biohydrogen (2-SOFC) were the least feedstock demanding pathways: in order to produce 1 MWh of electrical output from an SOFC, each fuel gas respectively requires 236.18 kg, 221.44 kg, and 217.05 kg of raw biomass to be processed. All fuels in *Table 5.1* had a better performance in SOFCs, with PEFCs performing best with fossil

hydrogen (RCb-PEFC) (242.80 kg/MWh electrical PEFC output). This is the current benchmark system for conventional fuel cell systems currently available for the widest variety of applications (mobile power, fuel cell vehicles, household units, *etc.*) [257].

The use of biowastes, such as agricultural residues and slurries, is a dominant choice for processes like anaerobic digestion and fermentation. These methods are used in waste to energy plants (which have to utilise intensive drying processes to increase the wet biomass' energy content – from 13 MJ/kg to 19MJ/kg), as well as in large scale agriculture (often cattle and swine farms). Additionally, waste lignocellulosic (woody) biomass (e.g. woody residues from sustainable forestry trimmings) are used extensively in thermochemical processes for syngas production (supercritical water gasification (SCWG) and gasification) for use in Integrated Gasification Combined Cycle power plants for heat and power production [207-209].

Syngas has been shown to perform well in SOFCs, with feedstock demands between 697.48 kg and 863.82 kg per MWh electrical SOFC output. When cleaned up into hydrogen gas, due to losses across the system, the feedstock demands are higher (typically over 1 tonne per MWh electrical fuel cell output). However, fermentation pathways have been estimated to require over 1.5 tonnes to achieve the same electrical output. For comparison, conventional syngas power generator (at 40% efficiency) will use over 2 tonnes of syngas per MWh of electricity generated [416].

In order to choose the most relevant processes for an LCA, the following was identified: (*i*) processes not covered extensively in literature (*Table 5.2*), and (*ii*) those that would directly produce methane and hydrogen (*Chapter 2*). The natural gas (RCa) and fossil hydrogen (RCb) reference cases were included in this search, as biogas (1a) and biomethane (1b), which are both produced by anaerobic digestion, are under discussion for natural gas grid

substitution [417]. The latter performed well in the previous biomass feedstock demand assessment (*Chapter 4*). An environmental impact assessment for the production of hydrogen from biomethane (1c) (the ideal fossil hydrogen reference case (RCb) alternative) in comparison to said reference case, would also further demonstrate its competitivity.

Ref.	Pathway	Fuel Gas	Number of publications and percentage contribution across pathways from ScienceDirect listings between 2008 and 2018									
			Unfiltered		Filters							
					Biomass		*Fuel Gas*		*Fuel Cell*		*Life Cycle Analysis*	
			No. of publications	% of pathway	No. of publications	% of pathway	No. of publications	% of pathway	No. of publications	% of pathway	No. of publications	% of pathway
	Anaerobic Digestion		48,074	100%	22,245	46%						
1a		Biogas					11,635	24%	4,036	8%	1,426	3%
1b		Biomethane					1,658	3%	807	2%	352	1%
1c		Hydrogen (BM)					10,759	22%	4,705	10%	1,821	4%
	Metabolic Processing		688,563	100%	56,313*	8%						
2		Biohydrogen					16,577	2%	6,091	1%	2,452	0.4%
	Dark Fermentation		29,451	100%	8,991	31%						
3a		Hydrogen					5,107	17%	2,906	10%	1,046	4%
	Light Fermentation		55,229	100%	16,091	29%						
3b		Hydrogen					8,456	15%	4,618	8%	1,950	4%
	Gasification		73,027	100%	33,460	46%						
4a		Syngas					9,457	13%	4,317	6%	1,518	2%
4b		Hydrogen (SG)					20,993	29%	9,846	13%	3,276	4%
	SCWG		6,560	100%	4,042	62%						
5a		Syngas					1,655	25%	1,068	16%	555	8%
5b		Hydrogen (SG)					3,343	51%	1,912	29%	919	14%
RCa	***Reference Case NG***	*De-sulphured Natural Gas*							*83,147*	*100%*	*24,301*	*29%*
RCb	***Reference Case H2***	*(Fossil) Hydrogen*							*48,606*	*100%*	*14,932*	*31%*

* the filter used for this specific pathway was 'Algae' to specifically find algal metabolic processing papers, as opposed to algal biomass, which is used in biodiesel production.

N.B. It is acknowledged that ScienceDirect is not the only source of journal publications, but when compared to Scopus and Google Scholar, it had the highest number of searchable papers. Therefore, ScienceDirect was chosen in hope of locating the most reliable statistics of relevant publications.

Table 5.2: 2008-2018 published research article results on ScienceDirect

Unfiltered Search: Only the biomass 'Pathway' (Anaerobic Digestion or SCWG) and 'Fuel Gas' (Biomethane or Hydrogen) were entered as search key words.

Filtered Searches: In addition to the above biomass 'Pathway' and 'Fuel Gas' example, more key words were individually added for more precise search results: 'Biomass', 'Fuel Gas', 'Fuel Cell', and 'Life Cycle Analysis'. These key words were entered as they are shown here, without pathway specific examples. The addition of these words separated gas systems from liquid fuel systems, and environmental impact studies from technoeconomic studies.

Metabolic processing had the highest number of publications, but these were found to mostly be research on biodiesel advances. Therefore, the 'Fuel Gas' filter was added to remove any biodiesel studies. This resulted in the number of publications dramatically reducing from nearly 670,000 to 16,500 (2% of total publications) and was further reduced to 0.4% with the addition of the 'LCA' filter.

The next largest pathway covered in literature was gasification, which is the preferred technique for producing syngas (4a) from dry biomass. Similarly, SCWG also produces syngas (5a), but utilising wet biomass, which would provide an interesting comparison against gasification to investigate how drying biomass affects the fuel gas production impact.

Conversely, the dark and light fermentation pathways (3a and 3b) are both well researched and many papers have conducted thorough LCAs on these topics, both individually and combined. However, fermentation is typically focus on ethanol production more than hydrogen, so they have not been included in this LCA, with efforts focussing on pathways directly producing usable gases.

The chosen pathways were subjected to Life Cycle Inventory Analysis (LCI), within the system boundaries set in *Section 5.2.1*, using the LCA software 'SimaPro' and the EcoInvent 3.2 database. Their environmental impact assessment was established within this software; impact categories and results will be presented in S*ection 5.2.2*.

5.2.1. System Boundaries

The system boundary for this study involved a 'Grave* to Cradle to Grave' analysis (*Figure 5.1*). This uses the wastes (i.e. 'Grave*' products) from a primary product system, where the *represents that the burdens from the primary production system are not allocated to

these fuel gas systems, as the Grave* products are a waste resource. The system includes the manufacture of raw gas, land use change and building of infrastructure/plant facilities, the production of manufacturing machines/reactors, processing into useable fuel gas, (including additional fuel clean-up for hydrogen gases, when applicable), and production of electricity ready for use, in either an SOFC or PEFC. Conversely, the gas well extraction and infrastructure for natural gas was also included to allow for a fair comparison.

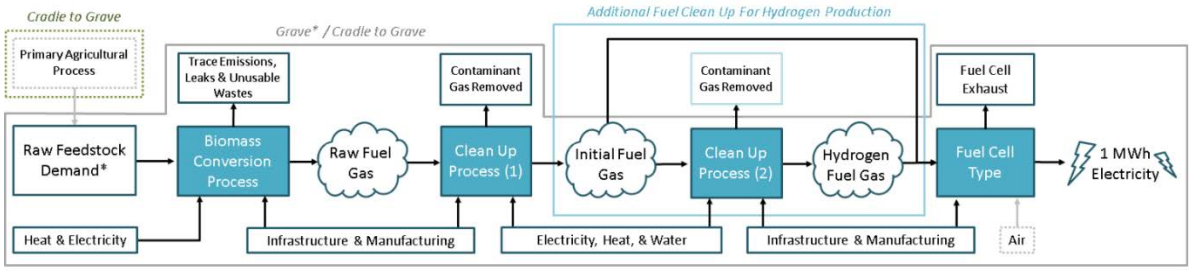


Figure 5.1: 1MWh SOFC system pathway, with system boundaries showing excluded (dotted lines) and included processes (solid lines)

In *Chapter 4, Figure 4.3* uses a similar variant of the overall process chain to show how the input data used in this chapter was calculated. *Figure 5.1* has additional inputs and outputs, which are used in the LCA inventory data, as well as demonstrating system boundaries outside the overall process chain scope.

5.3. Inventory Analysis

The functional unit used in this whole system assessment is 1 MWh electrical output from a fuel cell. To put this into perspective of electricity, on average, Ofgem states that a single UK households can consume an between 5 kWh and 20 kWh each day (*Table 5.1*) [418].

Table 5.3: Ofgem Typical Domestic Consumption Values in 2017 for Electricity, per household size
Source: [418]

	TDCVs	kWh yr^{-1}	kWh day^{-1}
Electricity: Profile Class 1	Low	1,900	5
	Medium	3,100	8
	High	4,600	13
Electricity: Profile Class 2	Low	2,500	7
	Medium	4,200	12
	High	7,100	19

In terms of carbon dioxide, 1 MWh electricity produced by the UK grid in 2018 produced 350 kg $CO_{2\ eq.}$ emissions, down from 450 kg $CO_{2\ eq.}$ in 2017, equating to a 21% reduction [419]. To put this into perspective, 350 kg $CO_{2eq.}$ also equates to around 1,940 miles driven by the average diesel passenger car (at 112 g/km driven [420] [421]), or growing 15 trees per year [422].

The allocated fuel gas demand for this functional unit varies per pathway, as well as the raw biomass feedstock (as explored in *Table 5.1*); system diagrams and mass balances for the pathways analysed are shown in *Figures 5.2 to 5.5.* The key processes and clean-up technologies for each pathway have been identified, as well as the key input quantities for each stage. To see how this data was calculated in greater detail, please see the Mass Balances Excel Spreadsheet in Appendix A.1 on the attached Thesis CD. This data has been entered into SimaPro LCA Software (version 8.2), utilising Allocated (Default) database data from EcoInvent 3.2 to fill in the gaps of more complex system components (machines and industrial processes).

As a general hypothesis, the greater number of low efficiency processes within the system, a greater difference in quantity should be seen between the starting raw feedstock demand and the produced fuel gas (prior to use in the fuel cell). However, if the processes have higher efficiencies, the loses through the whole system should not be significant enough to influence the raw feedstock demands. For instance, in *Figure 5.2*, 1a-SOFC, in order to produce 1 MWh of electrical output, the calculated raw feedstock demand of 236.18 kg/MWh. The anaerobic digester has an overall efficiency of 75%, which is demonstrated in the quantity of raw biogas produced (199.99 kg/MWh).

This clean-up process is typically completed using gas separation technology, like pressure swing adsorption (PSA) [423]. This technology has an 85% efficiency and is used to remove

contaminants [424-426] like hydrogen sulphide (H_2S) and silicon dioxide (SiO_2). Therefore, the fuel gas quality biogas loses another 15% of mass and creates a side-stream of removed mixed gases, which can be captured and sold to industry for clean-up. There are also alternative methods for removing biogas contaminants, like activated carbon filters [427], which is also utilised in the natural gas reference case (*Figure 5.5*, RCa-SOFC).

Much like Figure 5.1, Figures 5.2 to 5.5 start from left (raw biomass feedstock inputs) to right (fuel cell exhaust). The key data from *Table 5.1* and the mass balance spreadsheet (Appendix A.1) is presented at each stage, along with process efficiencies, to show how mass moves across the system, and where losses are accrued. Each system varies in complexity, depending on how many clean-up and/or reforming processes are required within each pathway.

In *Figure* 5.2, 1b-SOFC and 1c-SOFC, the biomethane and both hydrogen gases produced have higher lower heating values than that of biogas (13.89 kWh/kg and 33.34 kWh/kg, compared to 10 kWh/kg). Therefore, less quantities of biomethane and hydrogen are needed to produce the same 1 MWh output, but greater quantities of biogas are needed to produce the demanded fuel quantities as additional processes are required to extract the methane and hydrogen, respectively, contained within the biogas and biomethane. This, therefore, increases the amount of biogas and biomass feedstock required to make the final input to the fuel cell fuel gas. These factors can also be seen in *Figures 5.3 to 5.5*, as more complex process chains are realised.

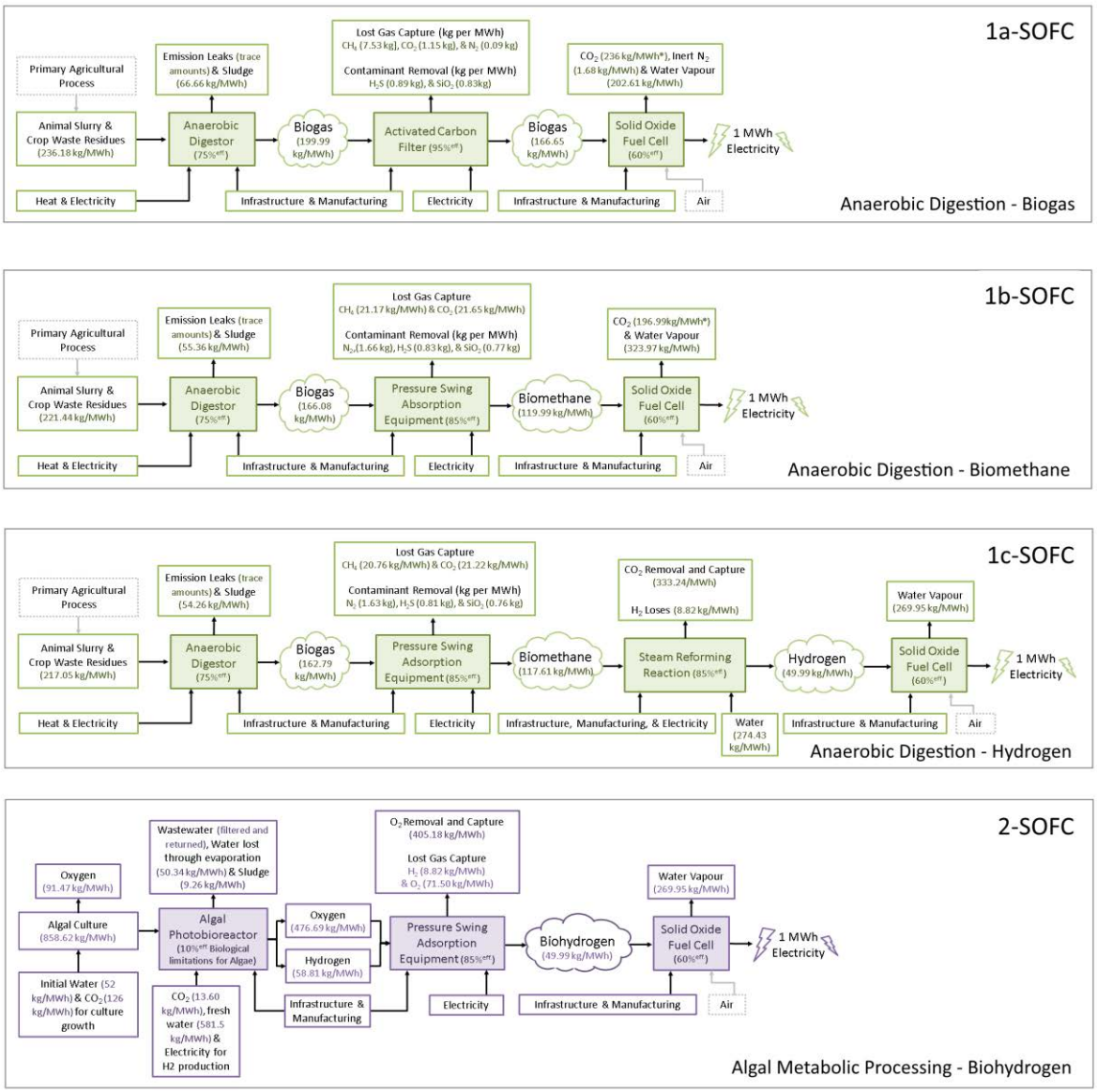


Figure 5.2: 1 MWh SOFC pathway flow diagram for: 1a-SOFC - anaerobic digestion biogas; 1b-SOFC - biomethane from biogas; 1c-SOFC - hydrogen from biomethane; and 2-SOFC - algal metabolic biohydrogen

In *Figure 5.2*, 2-SOFC is a simpler system due to the reactor gas produced being 66% hydrogen and 34% oxygen. Therefore, with use of a PSA, the oxygen can be removed, stored, and sold whilst the hydrogen comes out pure and ready for use in the SOFC. *Figure 5.4*, 2-PEFC, shows the same biohydrogen production processes for the PEFC system requirements.

Figure 5.3 presents the mass balances for the gasification and SCWG SOFC systems, both utilising syngas (4a-SOFC and 5a-SOFC) and hydrogen (4b-SOFC and 5b-SOFC). Across each

system, the major inputs and outputs have been identified, in addition to efficiencies for the main processes and clean-up/reforming techniques. The fuel gases are cleaned up and reformed using two of the more standard methods: an activated carbon filter and a PSA. Each has their own process efficiency for help in calculating the mass loses throughout the system, as well as the key gaseous outputs between each stage.

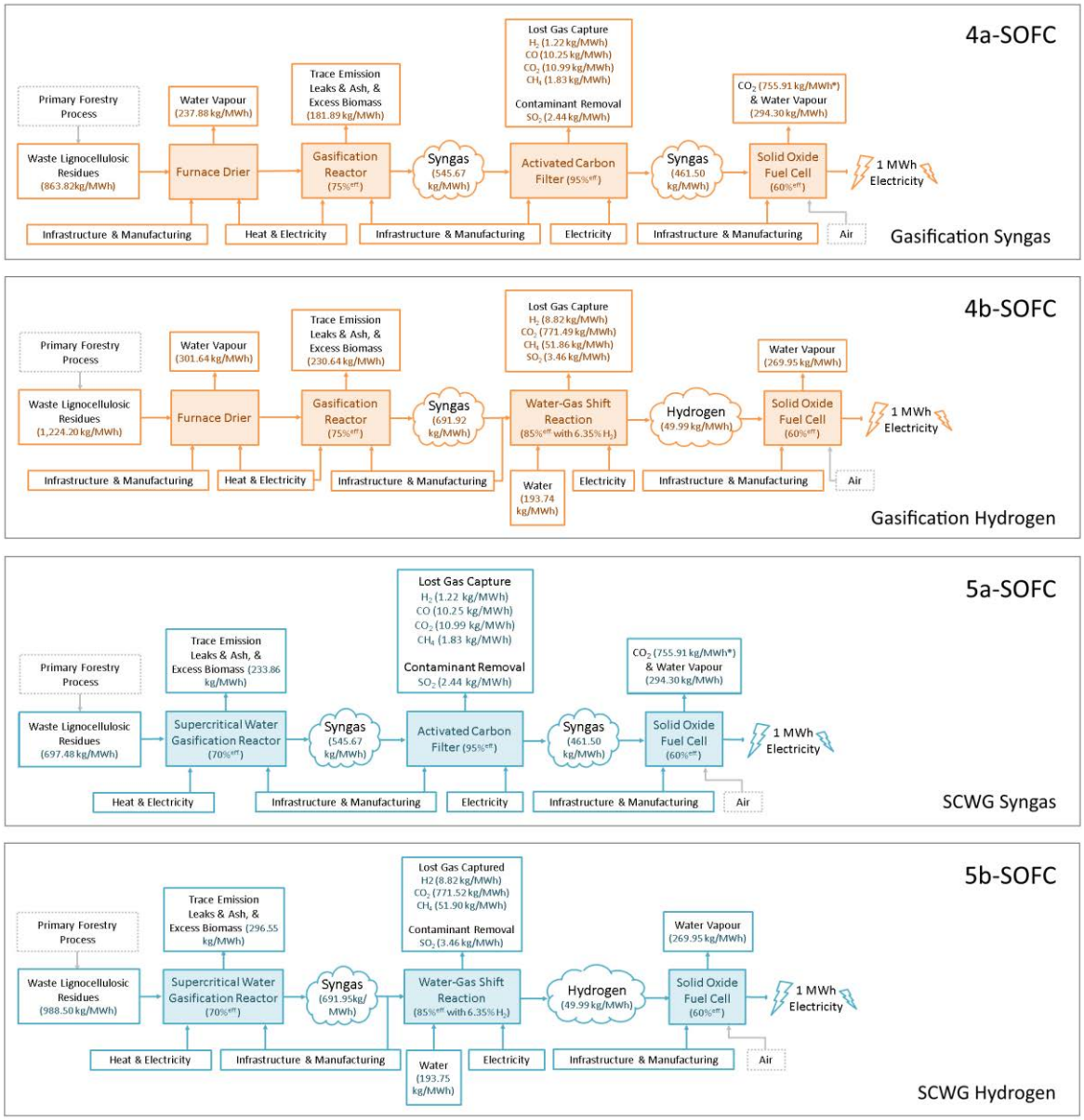


Figure 5.3: 1 MWh SOFC pathway flow diagram for: 4a-SOFC - gasification syngas; 4b-SOFC – hydrogen from gasification syngas; 5a-SOFC - SCWG syngas; and 5b-SOFC - hydrogen from SCWG syngas

For instance, in *Figure 5.4*, the top row of outputs for 1c-PEFC (e.g. 'Emission Leaks', 'Lost Gas Capture', 'Contaminant Removal', *etc.*) account for the 25% and 15% efficiency loses

in the AD Digestor, and PSA and steam methane reforming reaction, which have 75% and 85% efficiency. Therefore, assumptions are made that 75% and 85% of the desired gases are successfully produced and purified/reformed, and the remaining 25% and 15% (including the removed contaminants) leave the product system.

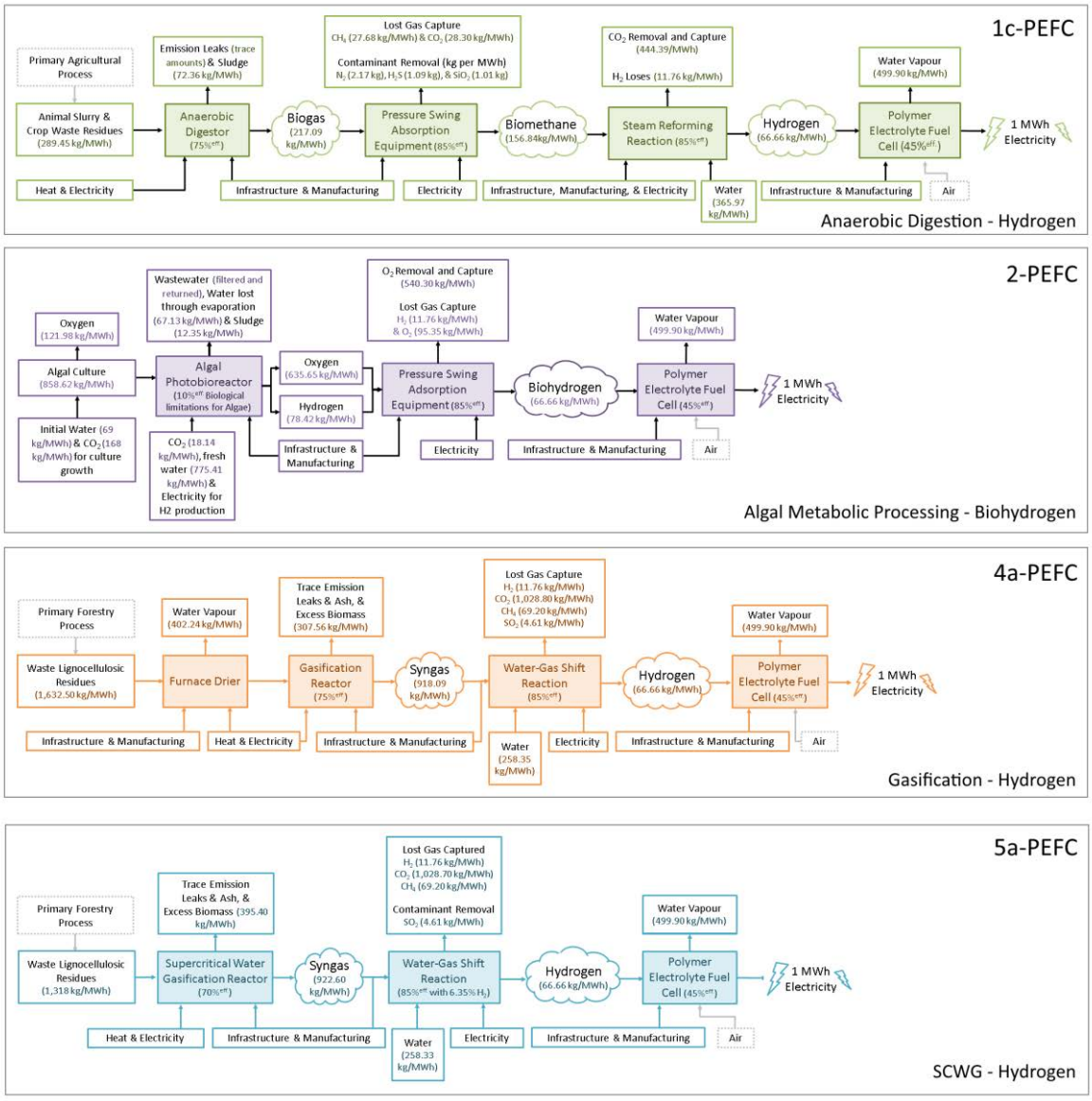


Figure 5.4: 1 MWh PEFC pathway flow diagram for: 1c-PEFC - hydrogen from biomethane; 2-PEFC - algal metabolic biohydrogen (2); 4b-PEFC - hydrogen from gasification syngas; and 5b-PEFC - hydrogen from SCWG syngas

In Figure 5.5, the fossil resource reference cases are presented. Unlike the biomass to gas pathways, there are no raw biomass feedstocks in these systems. Therefore, the left has amount of raw fossil natural gas demanded from the reserve (gas well), and the mass balance follows its 'sweetening' clean-up process to desulphured gas. Similarly, the

processes for producing hydrogen from steam reforming of natural gas is also included (RCb-SOFC and RCb-PEFC), which require an additional stage compared to the natural gas reference case (RCa-SOFC).

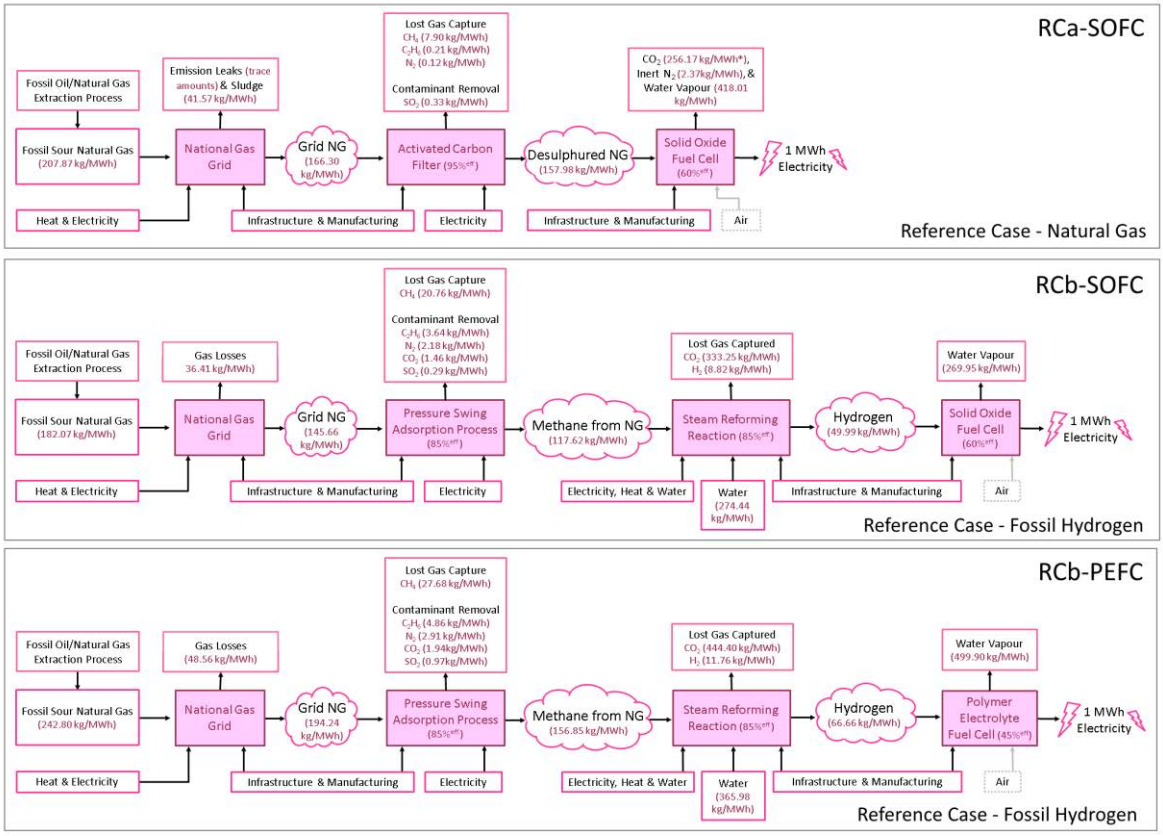


Figure 5.5: 1 MWh SOFC and PEFC pathway flow diagrams for the reference cases: RCa-SOFC - desulphured natural gas; RCb-SOFC - fossil hydrogen from natural gas; and RCb-PEFC - fossil hydrogen from natural gas

5.4. Impact Assessment

The process of assessing these systems within Simapro LCA software uses an inventory, compiled of the primary data calculated from first principals for the raw biomass feedstock and raw gas (*Chapter 4 and Appendix A.1 on the attached Thesis Disk*), with detailed process steps (*Figures 5.2 to 5.5,* above), and a fuel cell system made from data entries within the EcoInvent 3.2 database.

Each pathway inventory contains different types of data and substances that are linked to certain impact categories, which in turn are determined by a specific life cycle

methodology; for this research, CML-IA Baseline is being utilised. The SimaPro LCA software performs a complex calculation using the inventory data and its corresponding impact category data to produce the environmental impact results for each pathway assessed.

The following assessment (*Section 5.4.2*) looks at the production of the required raw gas input, which are needed to produce the fuel gas demand (*i*). Next, the clean-up/reforming/upgrading of these raw gases into the utilised fuel gases are assessed (*ii*). Finally, the whole system from SOFC and PEFC fuel cells running on the variety of biological pathway fuel gases investigated in *(iii)*, along with the fossil fuel reference cases. In addition, the substance contribution of all systems was investigated in order to identify the causes of hot spot processes and higher impact categories (*Section 5.5*) across the whole 1 MWh system for each individual fuel gas (*Figure 5.6*, Grave*/Cradle to Grave).

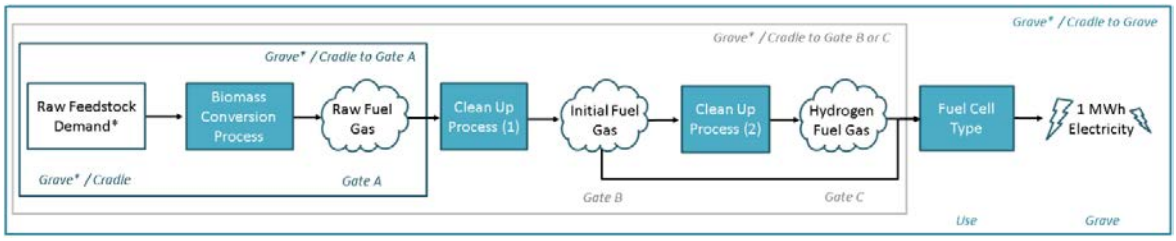


Figure 5.6: 1MWh SOFC system pathway, with system boundaries showing the core process chain.

* System boundaries begin with 'Grave' as the raw feedstocks are considered wastes in their primary system, the burdens of which are not allocated to the waste; considered a 'free resource'.

5.4.1. Impact Categories

ISO 14040 and 14044 state that at least three impact categories must be included in the impact assessment for a valid LCA [298]. Each impact category focuses on a different aspect of the environment, atmospheric and human emissions, and overall pollution. The CML-IA Baseline impact categories in *Table 5.4* were used in this assessment, for both producing results from the standard characterisation approach, as well as the EU25 normalisation approach.

Data normalisation involves dividing the characterisation data by the EU25 normalisation factor, converting from the standard impact category specific units to an 'EU domestic' unit, equating impacts to 'per person per year' equivalence [301], which demonstrates the personal magnitude of impacts [302]. This 'EU domestic' value is, for all-intensive purposes, dimensionless across all impact categories, allowing them to be compared directly and in more detail, including low quantity, but potent, impact categories.

Table 5.4: List of assessment impact categories and their individual emission units, normalisation factors, and subsequential environmental impacts

Source: [428]

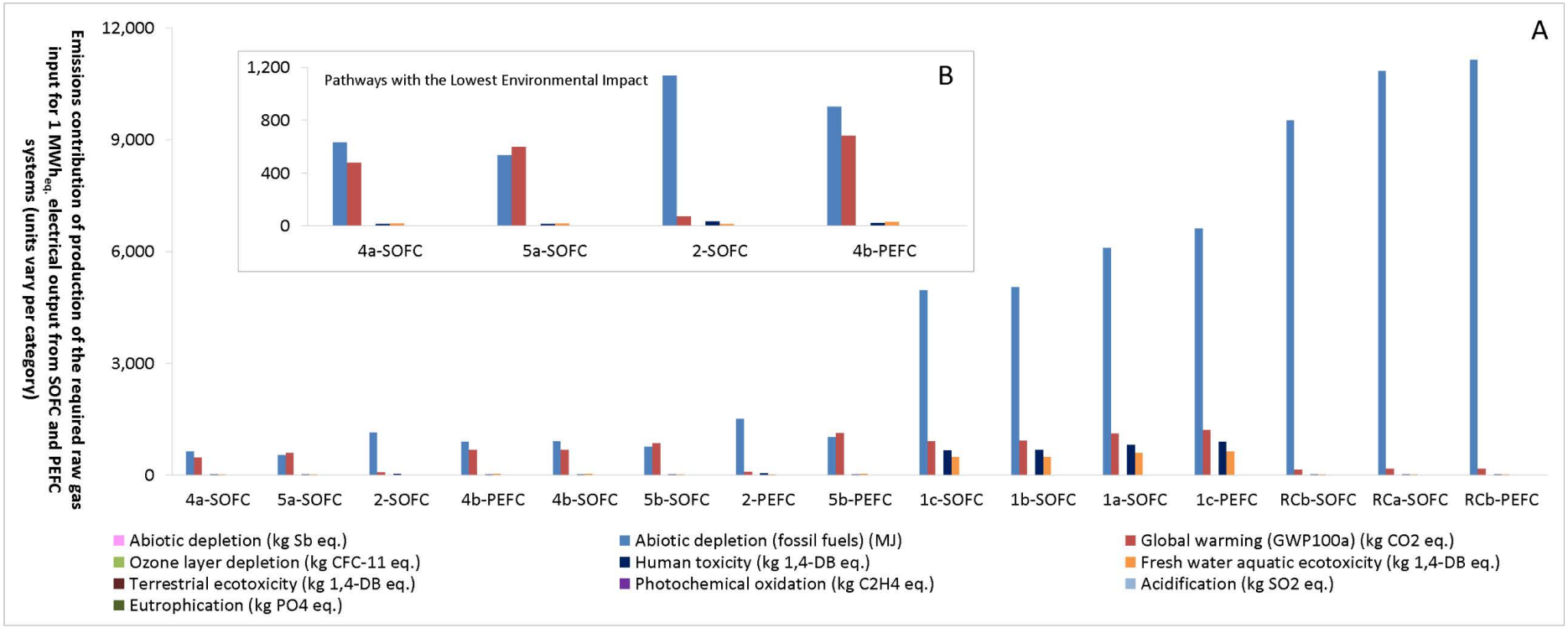
CML-IA Baseline Impact Category	Emissions Unit	EU25 Normalisation Factors	Environmental Impact
Abiotic Depletion	*kg* $SB_{eq.}$	1.18E-08	Resource depletion (minerals and metals measured in Antimony (Sb) eq.)
Abiotic Depletion (Fossil Fuels)	*MJ*	3.18E-14	Fossil fuel resource depletion (oil, gas, *etc.*)
Global Warming Potential (GWP^{100a})	*kg* $CO_{2eq.}$	1.99E-13	Greenhouse gas (CO_2, CH_4, *etc.*) emissions impact over 100 years.
Ozone Layer Depletion Potential	*kg CFC-11*$_{eq.}$	1.12E-08	Trichlorofluoromethane (CFC) gas emissions
Human Toxicity	*kg 1,4 Dichlorobenzene*$_{eq.}$	1.29E-13	Health concerns if exposed to humans (eyes and respiratory tract irritation)
Freshwater Aquatic Ecotoxicity Potential	*kg 1,4 Dichlorobenzene*$_{eq.}$	1.93E-12	Decreases aquatic biodiversity (chlorine, *etc.*)
Terrestrial Ecotoxicity Potential	*kg 1,4 Dichlorobenzene*$_{eq.}$	2.06E-11	Decreases land biodiversity (agrochem's *etc.*)
Photochemical Oxidation Potential	*kg* $C_2H_{4eq.}$	1.18E-10	Release of hazardous and toxic substances
Acidification Potential	*kg* $SO_{2eq.}$	3.55E-11	Atmospheric toxic, acidic gases released
Eutrophication Potential	*kg* $PO_{4eq.}$	7.58E-11	Excessive nutrients enter aquatic ecosystems

5.4.2. 1 $MWh_{eq.}$ Raw Gas Production

The raw gas comparison of 15 systems, from the conversion of the raw biomass feedstock to the raw gas production (*Figure 5.6, Grave*/Cradle to Gate A*), has been conducted by both characterisation and normalisation approaches and compiled into *Figures 5.7* and 5.8, respectively. The quantities used are dependent on the required input for the fuel gas demand, after purification, needed for the 1 MWh fuel cell electrical output functional unit. The three fossil reference case systems are also represented as a comparative baseline.

The data and legends are ordered by least impactful system (left) to most impactful system (right). The distinction of the largest affected impact categories vary depending on the type of approach used: Characterised results (*Figure 5.7*) are represented by the specific unit values for each impact category (Global Warming Potential (GWP^{100a}) = kg $CO_{2\ eq.}$, *etc.*); whereas the normalised results (*Figures 5.8 and 5.9*) have the EU25 normalisation factors from *Table 5.3* applied.

Full LCA impact assessment results for each pathway (individual characterised, normalised, and substance contribution analyses) for each fuel gas pathway are provided on the attached *Thesis Disk, Appendix A.1*.



Reference guide:

1a Anaerobic Digestion, Biogas
1b Anaerobic Digestion, Biomethane from Biogas
1c Anaerobic Digestion, Hydrogen from Biomethane
2 Metabolic Processing, Hydrogen
3a Dark Fermentation, Hydrogen
3b Light Fermentation, Hydrogen
4a Gasification, Syngas
4b Gasification, Hydrogen from Syngas
5a Supercritical Water Gasification, Syngas
5b Supercritical Water Gasification, Hydrogen from Syngas
RCa Reference Case, Natural Gas
RCb Reference Case, Hydrogen from Natural Gas

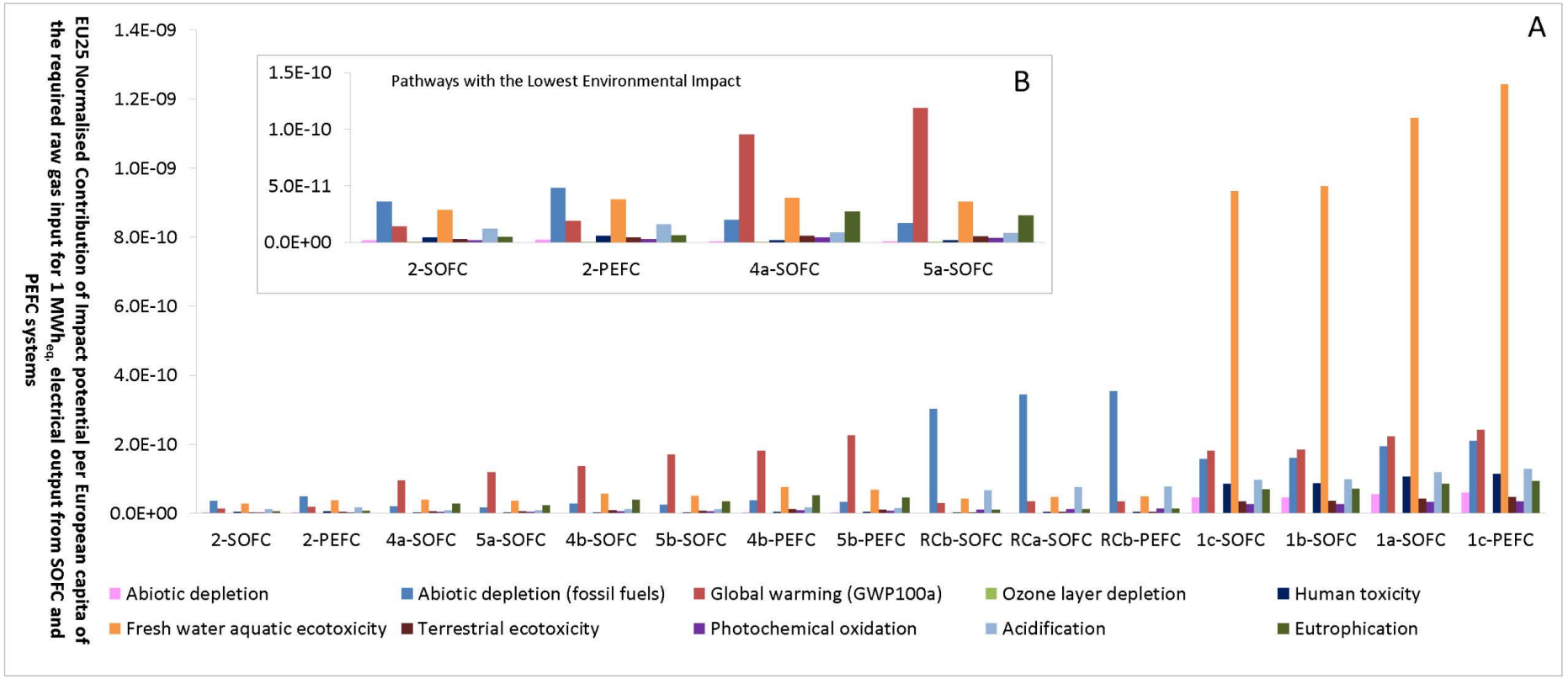
Figure 5.7: Standard characterised comparative impact assessment results for production of biologically derived raw gas input for 1 MWh$_{eq.}$ electrical output from SOFC and PEFC systems with fossil fuel reference cases. A – all systems; B – four lowest impacting systems (units dependent on impact category). (up to Gate B/C in Figure 5.6).

Figure 5.7, part A displays each impact category, with the tallest bars identifying categories and raw gas systems with the greatest impact (hotspots). The anaerobic digestion pathways and fossil fuel reference cases impacts are all dominated by Abiotic Depletion (Fossil Fuel) resource use; with the reference cases having the highest environmental impacts. *Figure 5.7, part B* focuses on the four impact categories with the lowest environmental impacts, which are therefore harder to see on the current axis; even with the normalised results in *Figure 5.8*, which uses the same ordering system of least impactful (left) to most impactful (right).

The results in *Figure 5.7* show the bare environmental impact for solely producing the raw gas from the core biomass conversion pathway, as well as the extracted raw (sour) natural gas for the fossil reference case systems (RCa and RCb). The four hydrogen from syngas systems (gasification (4b-SOFC and 4b-PEFC) and SCWG (5b-SOFC and 5b-PEFC), are within the least impactful lower half of the systems, with 4a-SOFC and 5a-SOFC as the two lowest impacting systems. Both biohydrogen methods (2-SOFC and 2-PEFC) are 3rd and 7th, followed by the anaerobic digestion systems, with the reference cases at the most impactful end.

Each system with waste/by-product revenue streams have undergone attributional system boundary extension, which includes the avoided products that they are capable of substituting. For instance, the two gasification systems (syngas (4a-SOFC) and hydrogen from syngas (4b-SOFC)) produce deisotoped (distilled) water as a by-product, which provides revenue when sold to industry. This by-product can be utilised as a substitute for distilled water and reduce demands on the market. This, therefore, results in avoided impacts. These systems have attributional system expansion factored in to include these benefits as a result of avoided products.

Biogas (1a-SOFC), biomethane (1b-SOFC), and hydrogen from biomethane (1c-SOFC and 1c-PEFC) have larger environmental impacts than the biohydrogen systems, partially due to the digestate that endangers local freshwater ecosystems, if released untreated, and the amount of gaseous emission leaks that occur from anaerobic digestors; No clear quantity is known, but up to 5% of all produced biogas is assumed to be lost, and up to 20% of all biomass feedstock is assumed to not breakdown/react correctly. Like gasification, they are long established technologies, but are mostly used on small to large scale farms and in rural areas.

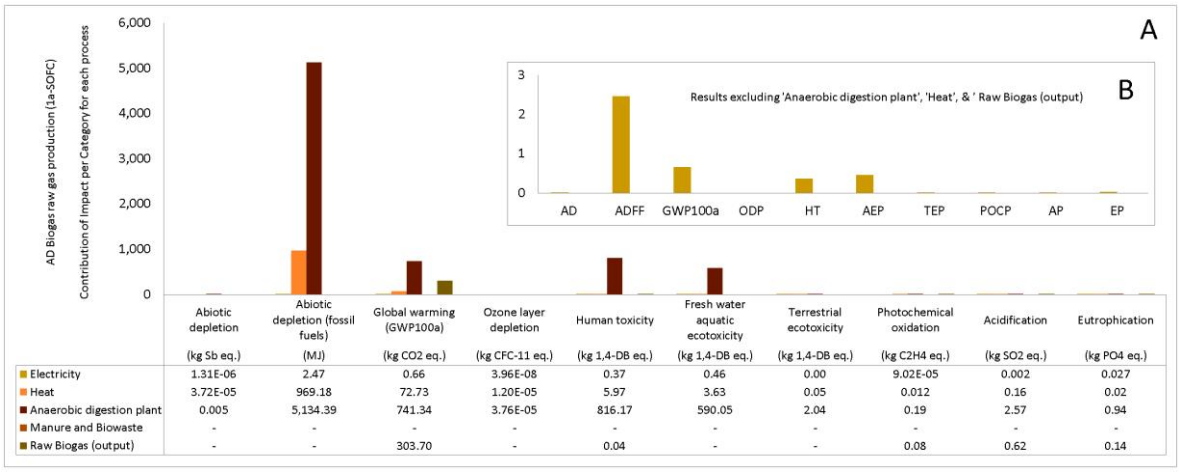


Reference guide:

1a Anaerobic Digestion, Biogas	**2** Metabolic Processing, Hydrogen	**4a** Gasification, Syngas	**5b** Supercritical Water Gasification, Hydrogen from Syngas
1b Anaerobic Digestion, Biomethane from Biogas	**3a** Dark Fermentation, Hydrogen	**4b** Gasification, Hydrogen from Syngas	**RCa** Reference Case, Natural Gas
1c Anaerobic Digestion, Hydrogen from Biomethane	**3b** Light Fermentation, Hydrogen	**5a** Supercritical Water Gasification, Syngas	**RCb** Reference Case, Hydrogen from Natural Gas

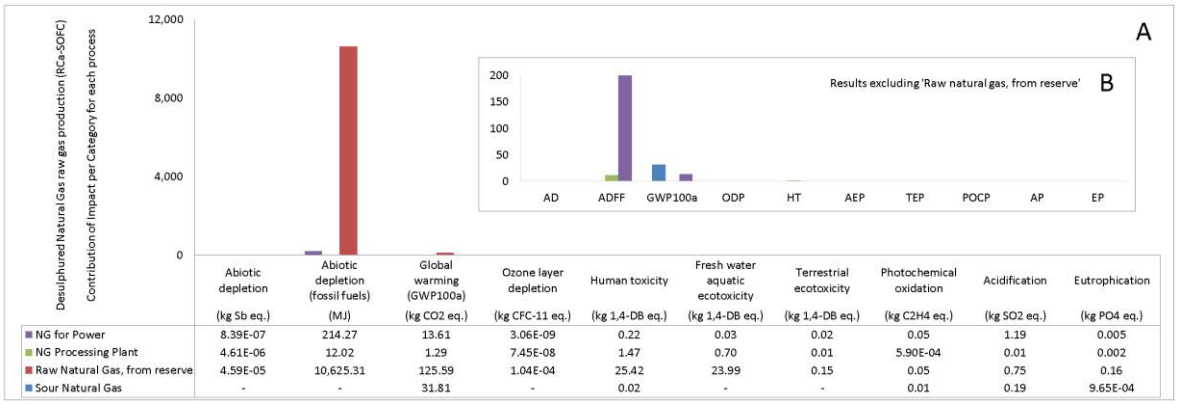
Figure 5.8: EU25 Normalised comparative impact assessment results for production of biologically derived raw gas input for 1 MWh$_{eq.}$ electrical output from SOFC and PEFC systems with fossil fuel reference cases. A – all systems; B – four lowest impacting systems (impact per EU capita). (up to Gate B/C in Figure 5.6.)

The anaerobic digestion plant itself was found to make up the majority of the biogas' impact (*see Figure 5.9*). In addition, the impacts of the fossil reference cases (RCa and RCb) are inclusive of extracting raw natural gas (*Figure* 5.10), resulting in the largest land use change, initial infrastructural impacts, and fossil fuel resource use of all the systems. The axis scale on *Figure 5.10, part A* is twice the size of *Figure 5.9, part A*, demonstrating the significant difference between the two systems.



	Abiotic depletion (kg Sb eq.)	Abiotic depletion (fossil fuels) (MJ)	Global warming (GWP100a) (kg CO2 eq.)	Ozone layer depletion (kg CFC-11 eq.)	Human toxicity (kg 1,4-DB eq.)	Fresh water aquatic ecotoxicity (kg 1,4-DB eq.)	Terrestrial ecotoxicity (kg 1,4-DB eq.)	Photochemical oxidation (kg C2H4 eq.)	Acidification (kg SO2 eq.)	Eutrophication (kg PO4 eq.)
Electricity	1.31E-06	2.47	0.66	3.96E-08	0.37	0.46	0.00	9.02E-05	0.002	0.027
Heat	3.72E-05	969.18	72.73	1.20E-05	5.97	3.63	0.05	0.012	0.16	0.02
Anaerobic digestion plant	0.005	5,134.39	741.34	3.76E-05	816.17	590.05	2.04	0.19	2.57	0.94
Manure and Biowaste	-	-	-	-	-	-	-	-	-	-
Raw Biogas (output)	-	-	303.70	-	0.04	-	-	0.08	0.62	0.14

Figure 5.9: Standard Characterisation impact assessment results of producing 1 $MWh_{eq.}$ of Raw Biogas from an Anaerobic Digestion plant (units dependent on impact category)



	Abiotic depletion (kg Sb eq.)	Abiotic depletion (fossil fuels) (MJ)	Global warming (GWP100a) (kg CO2 eq.)	Ozone layer depletion (kg CFC-11 eq.)	Human toxicity (kg 1,4-DB eq.)	Fresh water aquatic ecotoxicity (kg 1,4-DB eq.)	Terrestrial ecotoxicity (kg 1,4-DB eq.)	Photochemical oxidation (kg C2H4 eq.)	Acidification (kg SO2 eq.)	Eutrophication (kg PO4 eq.)
NG for Power	8.39E-07	214.27	13.61	3.06E-09	0.22	0.03	0.02	0.05	1.19	0.005
NG Processing Plant	4.61E-06	12.02	1.29	7.45E-08	1.47	0.70	0.01	5.90E-04	0.01	0.002
Raw Natural Gas, from reserve	4.59E-05	10,625.31	125.59	1.04E-04	25.42	23.99	0.15	0.05	0.75	0.16
Sour Natural Gas	-	-	31.81	-	0.02	-	-	0.01	0.19	9.65E-04

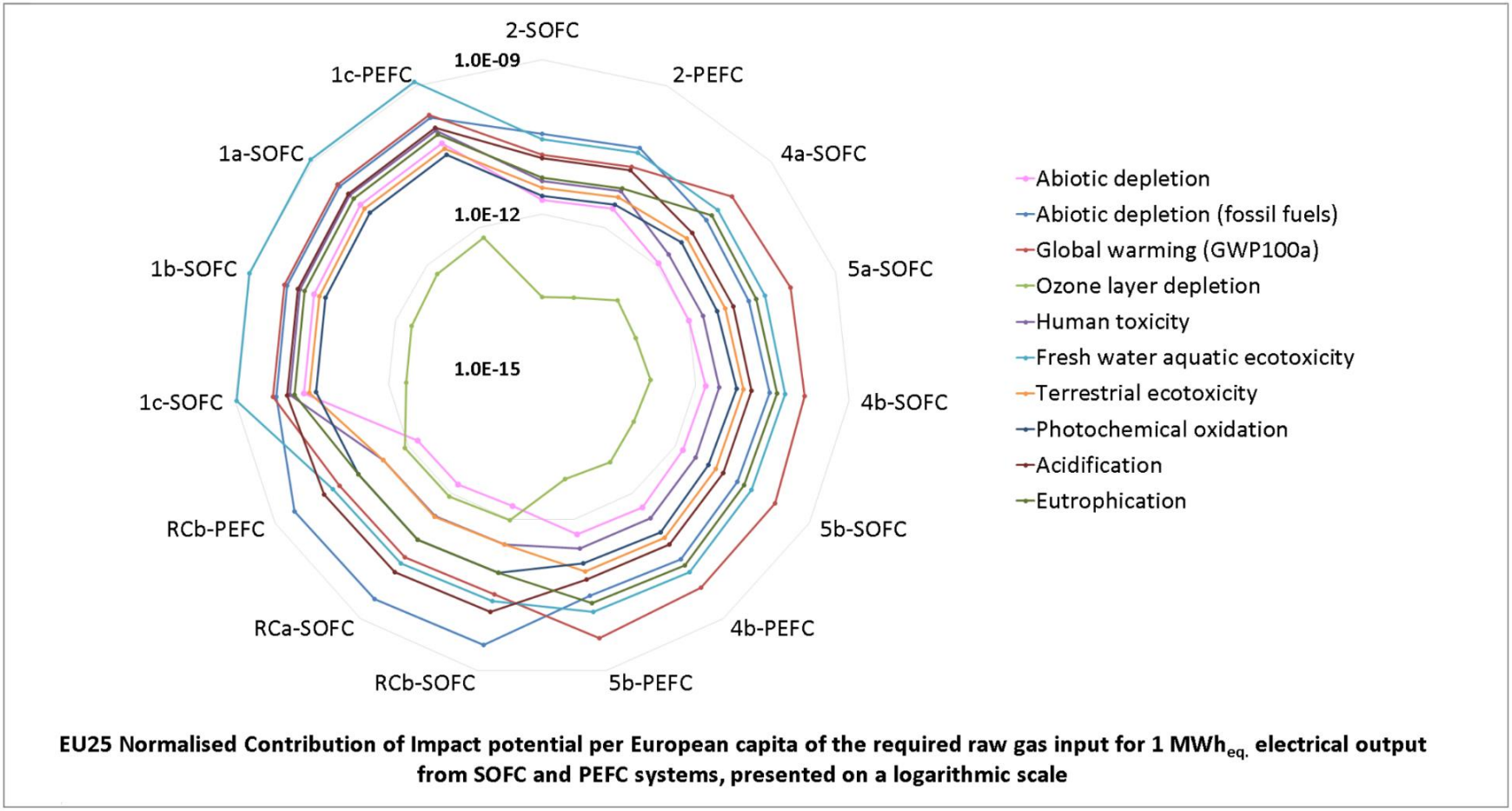
Figure 5.10: Standard Characterisation impact assessment results of extracting 1 $MWh_{eq.}$ of Raw Natural Gas from a reserve (units dependent on impact category)

On the other hand, the normalised results of the raw gas production systems (*Figure 5.8*) demonstrate that the biohydrogen systems actually have the lowest environmental impact, but also show a significant decrease in previously higher impacting systems (all fossil reference cases are now below all anaerobic digestion systems). The fossil fuel reference

cases have impacts specifically in Abiotic Depletion (Fossil Fuels), which is expected due to all three reference cases using sour natural gas, extracted from a gas well.

The anaerobic digestion systems all have increased Freshwater Aquatic Ecotoxicity impacts. For 1a-SOFC and 1b-SOFC, this is due to the amount of wastewater produced as part of the raw materials and mining processes, which is supposed to be sent to treatment tanks before released into the local water system. In addition, PEFC systems require more fuel gas than SOFC systems, as previously explored, and therefore has a higher impact due to more biomethane being processed. The Freshwater Aquatic Ecotoxicity impact also decreases from 1a-SOFC to 1c-SOFC because lower quantities of biogas are required for higher quality fuel gases, with 1c-PEFC being the exception due to more raw gas input being required.

On the whole, *Figure 5.8* is a good visual assessment of which system has the greatest environmental impact, whilst including the more potent influences of some lower quantity impact categories. An alternative perspective of presenting this same data would be to utilise a radar graph (*Figure 5.11*), which presents the systems in a way that shows the great impact category across all systems, and therefore the most influential environmental impact.



EU25 Normalised Contribution of Impact potential per European capita of the required raw gas input for 1 $MWh_{eq.}$ electrical output from SOFC and PEFC systems, presented on a logarithmic scale

Reference guide:

1a Anaerobic Digestion, Biogas	**2** Metabolic Processing, Hydrogen	**4a** Gasification, Syngas	**5b** Supercritical Water Gasification, Hydrogen from Syngas
1b Anaerobic Digestion, Biomethane from Biogas	**3a** Dark Fermentation, Hydrogen	**4b** Gasification, Hydrogen from Syngas	**RCa** Reference Case, Natural Gas
1c Anaerobic Digestion, Hydrogen from Biomethane	**3b** Light Fermentation, Hydrogen	**5a** Supercritical Water Gasification, Syngas	**RCb** Reference Case, Hydrogen from Natural Gas

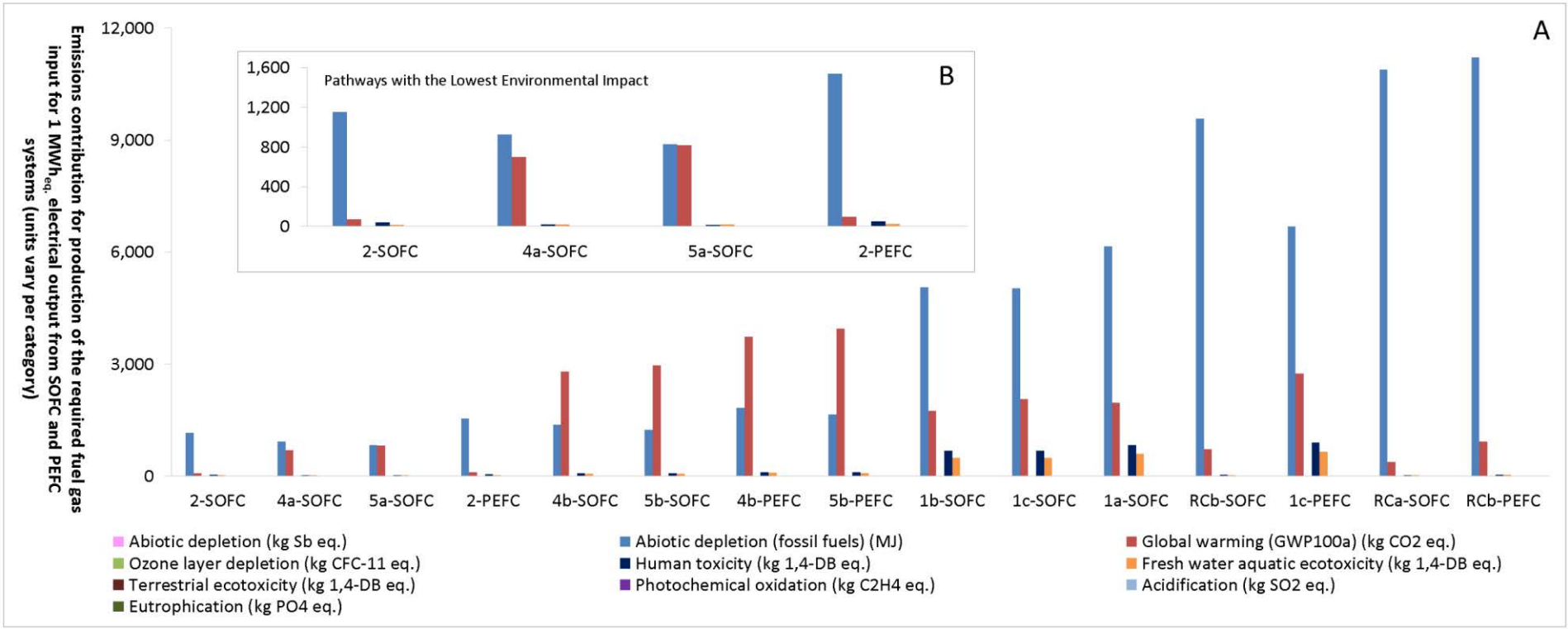
Figure 5.11: Normalised comparative impact assessment results for production of biologically derived raw gas input for 1 $MWh_{eq.}$ electrical output from SOFC and PEFC systems with fossil fuel reference cases. A – all systems; B – four lowest impacting systems (impact per EU capita). (up to Gate B/C in Figure 5.6).

The order of least to most impactful system runs clockwise around the radar graph, with the larger impact categories running around the outside of the graph. The centre represents impact categories with the least amount of impact, which in this case are: Ozone Layer Depletion Potential and Abiotic Depletion for all, if not most, raw gas systems. The most dominant categories are: GWP^{100a} across ten raw gas systems, Abiotic Depletion (Fossil Fuels) across 11 raw gas systems, and Freshwater Ecotoxicity Potential across nine raw gas systems.

This perspective is useful for the identification of dominant and subservient impact categories, and also provides a more visual representation of the most to least impactful assessed systems. However, due to the need of logarithmic scaling, this method of data presentation is not as precise and does not show the literal data results for these system models. Therefore, the rest of this assessment will utilise bar charts only.

5.4.3. 1 $MWh_{eq.}$ Fuel Gas Production

The next stage in this assessment involves the clean-up/reforming of the 1 $MWh_{eq.}$ of raw gas into useable fuels for both SOFC and PEFC technologies (*Figure 5.6*, Grave*/Cradle to Gate B or C). *Figure 5.12* demonstrates the true consequence of fuel gases, without the burdens of the fuel cell system (as assessed in *Section 5.4.4*). The impact of producing the fuel gases from their source raw gas has changed the system order (from low to high). Compared to *Figure 5.7,* in the lower impact systems in *Figure 5.12* (on the left of the graph) are 2-SOFC, 4a-SOFC, and 5a-SOFC, which demonstrates that some sub-processes involved in the production of the fuel gas itself have more of an influence on some systems than others.



Reference guide:

1a Anaerobic Digestion, Biogas
1b Anaerobic Digestion, Biomethane from Biogas
1c Anaerobic Digestion, Hydrogen from Biomethane
2 Metabolic Processing, Hydrogen
3a Dark Fermentation, Hydrogen
3b Light Fermentation, Hydrogen
4a Gasification, Syngas
4b Gasification, Hydrogen from Syngas
5a Supercritical Water Gasification, Syngas
5b Supercritical Water Gasification, Hydrogen from Syngas
RCa Reference Case, Natural Gas
RCb Reference Case, Hydrogen from Natural Gas

Figure 5.12: Standard characterised impact assessment results comparing the production of 1 MWh$_{eq.}$ fuel gases for SOFC and PEFC pathways with fossil fuel reference cases. A – all systems; B – four lowest impacting systems (units dependent on impact category). (up to Gate B/C in Figure 5.6.)

The characterised impact assessment results for the fuel gas production (*Figure 5.12)* once again identifies the Abiotic Depletion (Fossil Fuels) and GWP^{100a} impact categories as the most dominant. Some of these impacts have been carried over from the raw gas production stage, with additional impacts coming from the fuel gas production stage. This proves the expectations from these assessments in that 'intensive raw gas processing and clean-up increases the impact of the resulting fuel gas' [429]. For instance, the driver behind the additional impacts for the gasification and SCWG systems is the amount of carbon dioxide produced during the reforming of syngas into hydrogen via WGS (~200 kg CO_2/$MWh_{eq.}$ of fuel gas).

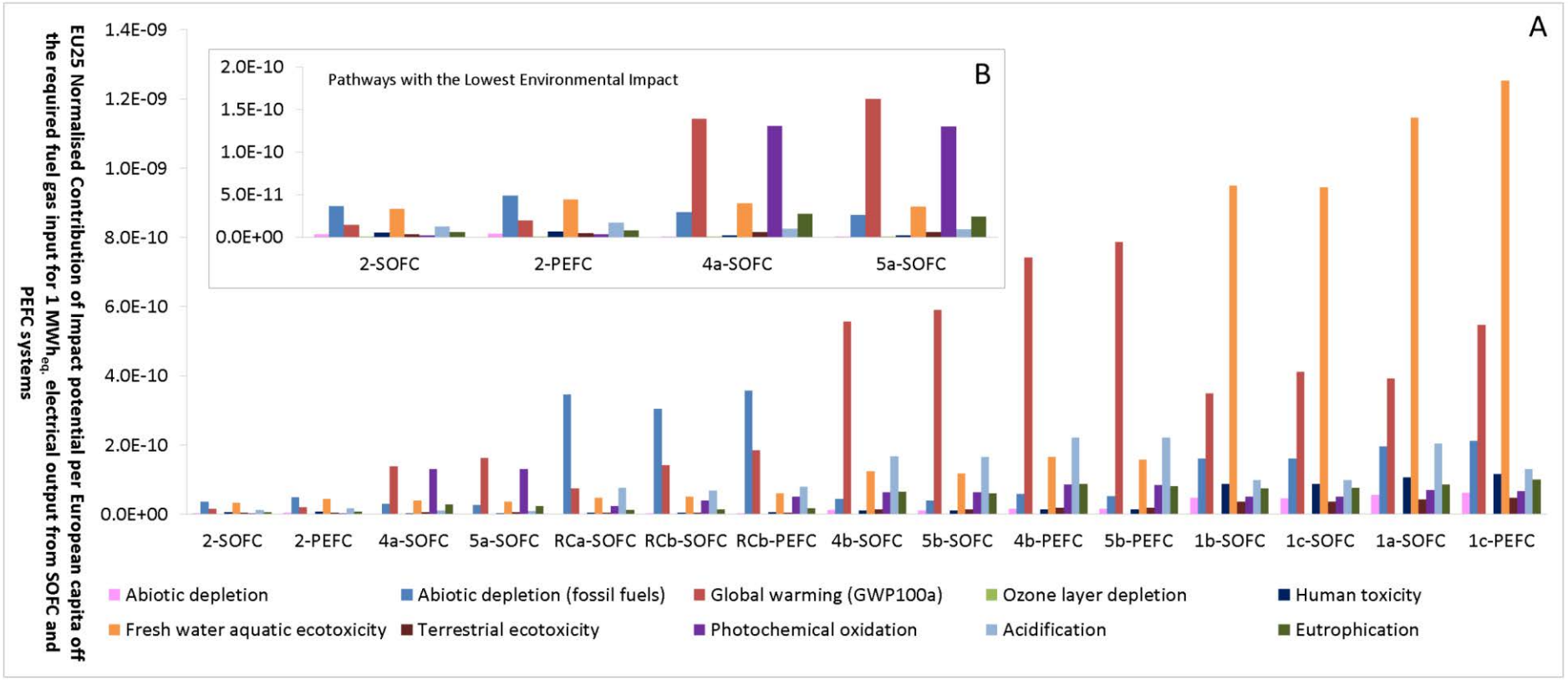
Gasification and SCWG technologies are two of the most developed biomass conversion technologies in this assessment. However, when utilising waste biomass feedstocks, the majority of both systems environmental impacts are from the collection and processing of said waste woody biomass. Coincidently, any system utilising this waste feedstock (i.e. combustion) would also accrue these impacts.

Hydrogen fuel gases (1c, 2, 4b, 5b, & RCb) have the highest fuel cell output (20 kWh/kg - 33.3 kWh/kg at 60% fuel cell efficiency [430, 431]). Therefore, they have a lower quantity demand for achieving the same 1 MWh electrical output (49.99 kg/MWh for SOFC and 66.66 kg/MWh for PEFC [68]), in comparison to lower LHV fuels like biogas (1a-SOFC) (166.65 kg/MWh - only for SOFC) and syngas (4a-SOFC and 5a-SOFC) (461.50 kg/MWh - only for SOFC) [68]. On the other hand, all fuel gases are required to be purified or cleaned-up before they can be used, due to contaminants, such as sulphur and chlorine, poisoning the fuel cell catalyst [358].

The Freshwater Aquatic Ecotoxicity Potential impact is mostly unchanged for all anaerobic digestion systems, which confirms that the impact drivers originate in the raw biogas production, as opposed to the additional impacts driven by clean-up/reforming.

The lowest environmental impact fuel gas production systems in *Figure 5.12* remain to be SOFC biohydrogen (2-SOFC) and syngas (gasification, 4a-SOFC and SCWG, 5a-SOFC), with the PEFC biohydrogen system (2-PEFC) varying in position between *Figures 5.12* and *5.13,* demonstrating some differences between Characterised results and Normalised results. The greater number of low impact SOFC pathways is expected, as SOFCs have a higher efficiency [432] and therefore a lower fuel gas demand. SOFCs internal reforming feature allows a greater variety of fuels to choose from, so less intensively processed fuels are accessible [432, 433]. Hydrogen directly sourced from biological processes, like algal metabolic processing (2-SOFC and 2-PEFC), has been found to be prominent in recent research (as seen in *Table 5.2*).

In *Figure 5.12*, the hydrogen from biomethane (1c-PEFC and 1c-SOFC) and biogas (1a-SOFC) systems are still amongst the highest impactors, alongside the reference case systems. Hydrogen from syngas (gasification (4b-SOFC and 4b-PEFC) and SCWG (5b-SOFC and 5b-PEFC)) are shown to vary in performance around the fossil natural gas reference cases, which is one of the next highest impacting systems after hydrogen from syngas; thus strengthening the argument to supplement the fossil based national gas grid with biological sourced gases [434-436]. An example of this would be an additional assessment of 1a-SOFC, with the inclusion of substituting natural gas (avoided products of equivalent quantities) and the rival RCa-SOFC system (*see Section 5.5.1, ii*).



1a Anaerobic Digestion, Biogas
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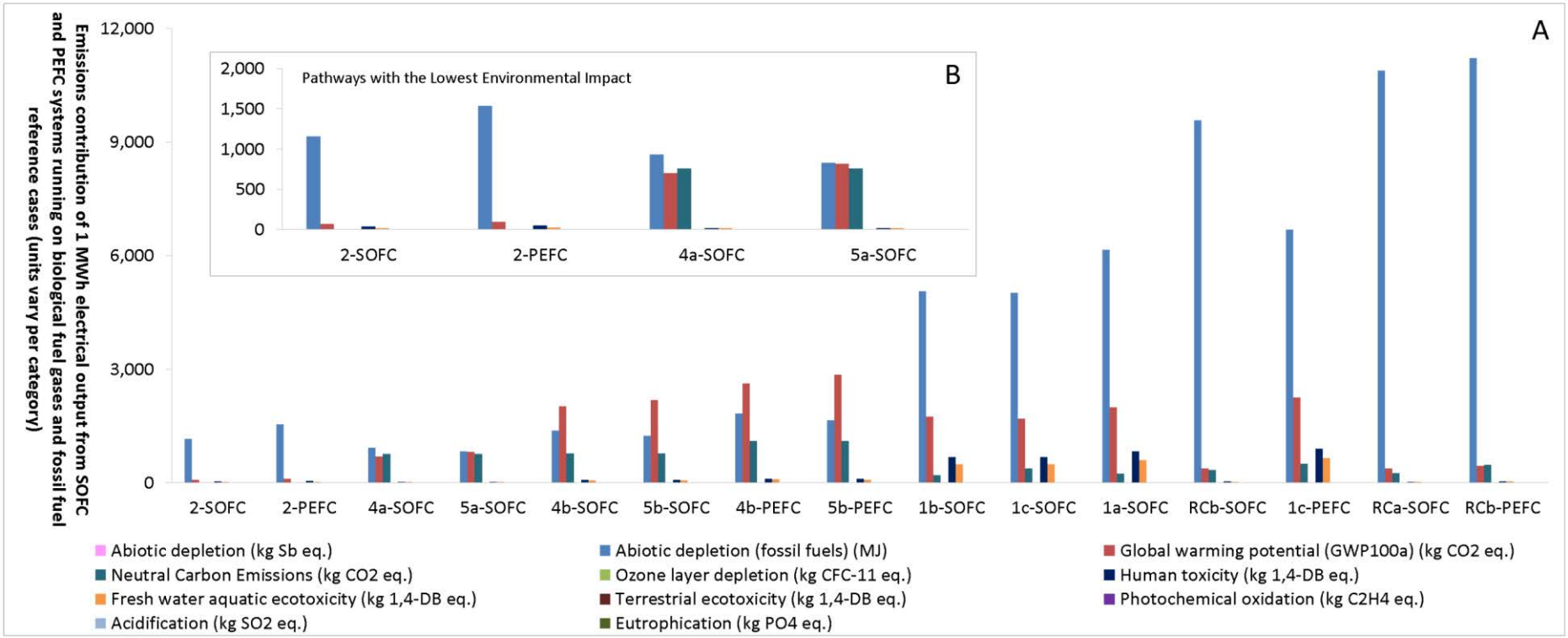
3b Light Fermentation, Hydrogen
4a Gasification, Syngas
4b Gasification, Hydrogen from Syngas
5a Supercritical Water Gasification, Syngas
5b Supercritical Water Gasification, Hydrogen from Syngas
RCa Reference Case, Natural Gas
RCb Reference Case, Hydrogen from Natural Gas

Figure 5.13: EU25 Normalised impact assessment results comparing the production of 1 MWh$_{eq.}$ fuel gases for SOFC and PEFC pathways with fossil fuel reference cases. A – all systems; B – four lowest impacting systems (impact per EU capita). (up to Gate B/C in Figure 5.6.)

5.4.4. 1 MWh Output Whole System Comparison

The most predominant impact categories in the whole system analysis, across both characterisation and normalised approaches (in no particular order) are Abiotic Depletion (Fossil Fuels), GWP100a, and Freshwater Aquatic Ecotoxicity Potential. These impact categories are driven by the amount of resources required for the fuel cells, production of infrastructure and materials for machines, manufacturing, energy, *etc.*, in addition to the raw gas clean-up and reforming processes, the latter of which also require water. As seen in the previous assessments, most systems assessed attribute their emission impacts to similar intensive processes.

In the whole system analysis, the biohydrogen (2-SOFC and 2-PEFC) systems are now the lowest two impacting pathways, as seen in both *Figures 5.14 and 5.15*, followed by the SOFC syngas pathways (gasification (4a-SOFC) and SCWG (5a-SOFC)). Two of the fossil reference cases (RCa-SOFC and RCb-PEFC) remain the highest impact systems in all the characterised results (*Figures 5.7, 5.12,* and *5.14)*, whilst they have consecutively been median impact systems in all the normalised results (*Figures 5.8, 5.13,* and *5.14*). This is because the EU25 normalisation factor has attributed GWP^{100a} and Freshwater Aquatic Ecotoxicity Potential to be more environmentally impactful than Abiotic Depletion (Fossil Fuels). Therefore, systems with greater impacts remain to be the anaerobic digestion pathways (1c-PEFC, 1a-SOFC, 1c-SOFC, and 1b-SOFC); which under the deeper analysis of *Section 5.5*, was found to be driven by the anaerobic digester reactor.



Reference guide:

1a Anaerobic Digestion, Biogas
1b Anaerobic Digestion, Biomethane from Biogas
1c Anaerobic Digestion, Hydrogen from Biomethane
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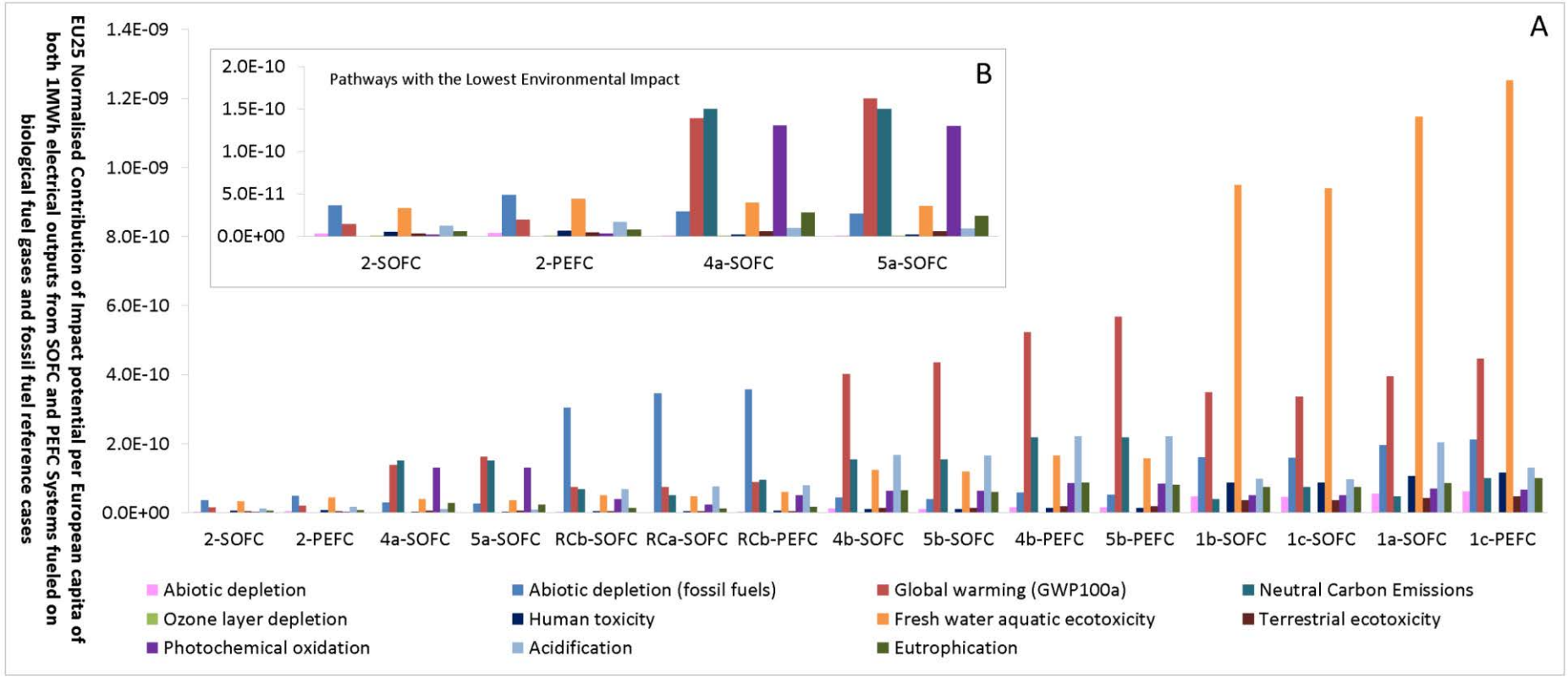
3b Light Fermentation, Hydrogen
4a Gasification, Syngas
4b Gasification, Hydrogen from Syngas
5a Supercritical Water Gasification, Syngas
5b Supercritical Water Gasification, Hydrogen from Syngas
RCa Reference Case, Natural Gas
RCb Reference Case, Hydrogen from Natural Gas

Figure 5.14: Standard characterised impact assessment results comparing the 1 MWh electrical output from SOFC and PEFC systems running on biologically derived fuel gases with fossil fuel reference cases. A – all systems; B – four lowest impacting systems (units dependent on impact category). (up to Gate A in Figure 5.6.)

All four hydrogen from syngas pathways for both SOFC and PEFC systems are showing the largest contributions to be GWP^{100a}, due to the amount of water required to produce the hydrogen fuel gas through water-gas shift reaction; which results in large quantities of carbon dioxide. However, it must be acknowledged that the carbon dioxide emissions from all hydrogen from syngas pathways are dominated by biogenic carbon molecules; which was previously sequestrated from the atmosphere during the biomass growth and are therefore carbon-neutral.

When considering the temporal effect of short term carbon sequestration, carbon dioxide emissions are carbon-neutral if the fuel gas has been sourced from biomass. Conversely, fossil resources have long term temporal impacts as they have been removed from the carbon cycle for too long to still have a neutral effect. Therefore, fuel cells with net carbon emissions only result from using fossil resources such as town gas or natural gas, both in the fuel stream itself, and any ancillary energy consuming steps involved in processing the fuel gas which are driven by fossil sources.

In *Figures 5.14 and 5.15*, there is an additional impact column that represents the 'Neutral Carbon Emissions' that come out of the fuel cell. This is made up of the kg CO_2 that is produced as part of the internal reforming and use of fuel gases that contain carbon (biogas, biomethane, syngas, and natural gas). This data was calculated using the chemical reaction equations as part of the mass balance (*available on the Thesis Disk, Appendix A.1*). If the exhaust gases were captured and stored, instead of released, these carbon bars could instead be shown on a negative axis, as the carbon is being removed from the carbon cycle, and therefore results in negative carbon emissions. On the other hand, natural gas contains carbon that has been removed from the carbon cycle for millennia, and therefore has a more damaging effect on the atmosphere when it is released.



Reference guide:

1a Anaerobic Digestion, Biogas
1b Anaerobic Digestion, Biomethane from Biogas
1c Anaerobic Digestion, Hydrogen from Biomethane
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4b Gasification, Hydrogen from Syngas
5a Supercritical Water Gasification, Syngas
5b Supercritical Water Gasification, Hydrogen from Syngas
RCa Reference Case, Natural Gas
RCb Reference Case, Hydrogen from Natural Gas

Figure 5.15: Normalised impact assessment results comparing the 1 MWh electrical output from SOFC and PEFC systems running on biologically derived fuel gases with fossil fuel reference cases. A – all systems; B – four lowest impacting systems (impact per EU capita). (up to Gate A in Figure 5.6.)

The environmental impact of the reference cases is due to the use of finite fossil resources. Conversely, 1c-PEFC and 1a-SOFC are predominately from the raw biogas production and the steam methane reforming process, which, like WGS for syngas, also uses water and heat to reform the biomethane into hydrogen. The degree of impact across the different impact categories look almost the same, with Abiotic Depletion (Fossil Fuels) and GWP^{100a} still being the highest impact categories. This demonstrates that the environmental impact of the fuel cell system itself, including its maintenance, gas storage, *etc*. is negligible in comparison to the fuel gas production for most systems and more impactful for others (4a-SOFC and 5a-SOFC).

When comparing the impact assessment of the raw gas and fuel gas analyses to the whole system impacts, the production of raw gases and processes for cleaning and/or reforming the gas continue to dominate across every system, as seen with the unchanging axis from raw gas (*Figure 5.7*), to whole system (*Figure 5.14*).

Therefore, assessing different system boundaries of the same system allow more detailed results to be generated, especially when comparing characterisation and normalisation approaches. Using this approach has also demonstrated the variations caused by moving a system boundary and how more intensive stage processes have a major impact on the results. The final stage of this research will assess the substances and sub-processes driving some of these hotspot systems and impacts.

5.5. Impact Contribution

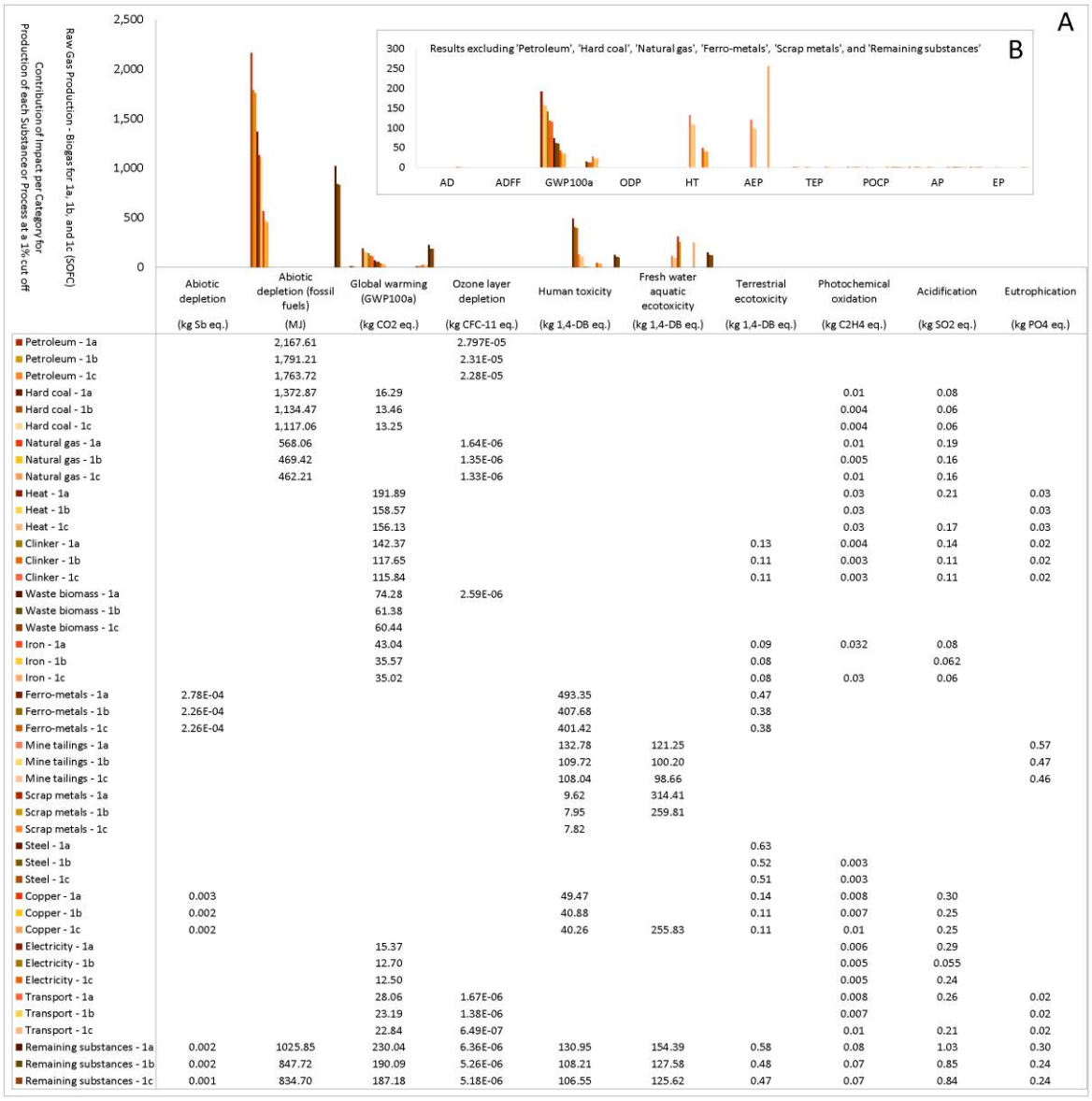
Across *Section 5.4*, there were several specific SOFC systems that were consistently both high and low impactors. PEFC systems were consistently more environmentally impactful, though, because they require more fuel to run due to lower efficiency and higher effort to

produce higher purity hydrogen fuel. However, PEFCs have some materials (platinum, steel, *etc.)* that typically drive most of their environmental impact [437]. Therefore, by focusing on SOFC system specific raw gases from across different degrees of impact, a deeper individual assessment can be undertaken to isolate the substances contributing to areas of concern – also known as hot spots.

5.5.1. Anaerobic Digestion

As a leading choice for incorporating biomass derived fuels into the existing national gas grid, biogas produced by anaerobic digestion has multiple fuel gas applications, each with a limited degree of clean-up and reforming. However, these processes can increase the environmental footprint of the end product, as previously seen.

The core impacts are from: the anaerobic digestion plant, driven by the land use change and building resources for infrastructure, and heat generation to maintain optimum conditions (mesophilic for cultures at ~35°C or thermophilic at ~55°C [131, 132, 147]). However, not all digesters are completely airtight, so trace leak emissions have also been accounted for within the anaerobic digestion plant subprocess. *Figure 5.16* is made up of the substances and processes for making the anaerobic digester, which dominates the raw biogas impacts; the majority of which is fossil fuel resource use and metal mining. Clinker (a coke-like by-product) is also produced when the biomass feedstock isn't subjected to the correct conditions to breakdown properly (or if dirt is added to the digester) [438]. This is found within the digestate sludge and accumulates in settlement ponds/lagoons/tanks.



Production of each Substance or Process at a 1% cut off / Contribution of Impact per Category for Raw Gas Production - Biogas for 1a, 1b, and 1c (SOFC)	Abiotic depletion (kg Sb eq.)	Abiotic depletion (fossil fuels) (MJ)	Global warming (GWP100a) (kg CO2 eq.)	Ozone layer depletion (kg CFC-11 eq.)	Human toxicity (kg 1,4-DB eq.)	Fresh water aquatic ecotoxicity (kg 1,4-DB eq.)	Terrestrial ecotoxicity (kg 1,4-DB eq.)	Photochemical oxidation (kg C2H4 eq.)	Acidification (kg SO2 eq.)	Eutrophication (kg PO4 eq.)
Petroleum - 1a		2,167.61		2.797E-05						
Petroleum - 1b		1,791.21		2.31E-05						
Petroleum - 1c		1,763.72		2.28E-05						
Hard coal - 1a		1,372.87	16.29					0.01	0.08	
Hard coal - 1b		1,134.47	13.46					0.004	0.06	
Hard coal - 1c		1,117.06	13.25					0.004	0.06	
Natural gas - 1a		568.06		1.64E-06				0.01	0.19	
Natural gas - 1b		469.42		1.35E-06				0.005	0.16	
Natural gas - 1c		462.21		1.33E-06				0.01	0.16	
Heat - 1a			191.89					0.03	0.21	0.03
Heat - 1b			158.57					0.03		0.03
Heat - 1c			156.13					0.03	0.17	0.03
Clinker - 1a			142.37				0.13	0.004	0.14	0.02
Clinker - 1b			117.65				0.11	0.003	0.11	0.02
Clinker - 1c			115.84				0.11	0.003	0.11	0.02
Waste biomass - 1a			74.28	2.59E-06						
Waste biomass - 1b			61.38							
Waste biomass - 1c			60.44							
Iron - 1a			43.04				0.09	0.032	0.08	
Iron - 1b			35.57				0.08		0.062	
Iron - 1c			35.02				0.08	0.03	0.06	
Ferro-metals - 1a	2.78E-04				493.35		0.47			
Ferro-metals - 1b	2.26E-04				407.68		0.38			
Ferro-metals - 1c	2.26E-04				401.42		0.38			
Mine tailings - 1a					132.78	121.25				0.57
Mine tailings - 1b					109.72	100.20				0.47
Mine tailings - 1c					108.04	98.66				0.46
Scrap metals - 1a					9.62	314.41				
Scrap metals - 1b					7.95	259.81				
Scrap metals - 1c					7.82					
Steel - 1a							0.63			
Steel - 1b							0.52	0.003		
Steel - 1c							0.51	0.003		
Copper - 1a	0.003				49.47		0.14	0.008	0.30	
Copper - 1b	0.002				40.88		0.11	0.007	0.25	
Copper - 1c	0.002				40.26	255.83	0.11	0.01	0.25	
Electricity - 1a			15.37					0.006	0.29	
Electricity - 1b			12.70					0.005	0.055	
Electricity - 1c			12.50					0.005	0.24	
Transport - 1a			28.06	1.67E-06				0.008	0.26	0.02
Transport - 1b			23.19	1.38E-06				0.007		0.02
Transport - 1c			22.84	6.49E-07				0.01	0.21	0.02
Remaining substances - 1a	0.002	1025.85	230.04	6.36E-06	130.95	154.39	0.58	0.08	1.03	0.30
Remaining substances - 1b	0.002	847.72	190.09	5.26E-06	108.21	127.58	0.48	0.07	0.85	0.24
Remaining substances - 1c	0.001	834.70	187.18	5.18E-06	106.55	125.62	0.47	0.07	0.84	0.24

Figure 5.16: Substance contribution impact assessment results for 1 $MWh_{eq.}$ of biogas (1a), for biomethane, post PSA (1b), and for hydrogen from biomethane (1c); all for use in SOFCs. A – whole system; B – whole system excluding 'Petroleum', 'Hard coal', 'Natural gas', 'Ferro-metals', 'Scrap metals', and 'Remaining substances', to show smaller scale (units dependent on impact category)

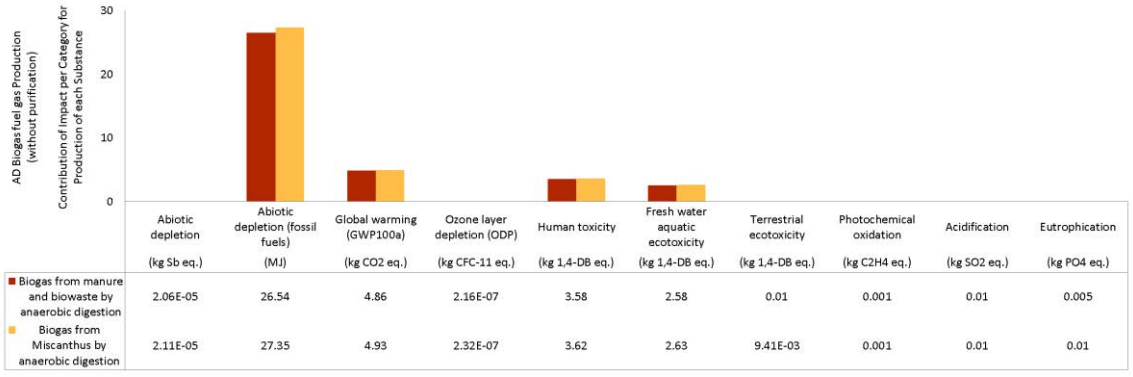
Manure and agricultural biowastes are the assumed inputs for this process. These wastes are normally composted or undergo uncapped anaerobic digestion, which releases greenhouse gases into the atmosphere [439] with both methods resulting in an organic fertiliser substitute that the farms use to supplement the fields. These are standard procedures as slurries and sludges must be reduced to below a biological oxygen demand threshold, in addition to having a valid landspreading permit [440]. This prevents the ecological damage caused by excessive amounts of nutrients leaching from the land –

Freshwater Ecotoxicity Potential and Eutrophication Potential are examples of these resulting impacts. Therefore, by harnessing the gases emitted naturally from this treatment, the gaseous products from anaerobic digestion can be considered a 'free' resource, with the digester sludge being appropriate for spreading on fields, so there are no losses to the farmers.

Regarding the drivers of these impacts, Abiotic Depletion (Fossil Fuels), of oil and coal in particular, is driving the majority of the total environmental burdens. Additionally, *Figure 5.16, part B*, which are the results excluding 'petroleum', hard coal', 'natural gas', 'ferro-metals', 'scrap metals', and 'remaining substances', allow for the smaller substance and process impacts to be seen. Here, GWP^{100a} drives the smallest impacts, predominantly heat, clinker, waste biomass, and iron.

i. Feedstock Substitutes

Outside of this substance contribution impact assessment, the raw feedstock sources can also influence the environmental performance for producing fuel gases from anaerobic digestion biogas. For example, *Figure 5.17* demonstrates the subtle difference of using biowaste and energy crops, like miscanthus, in anaerobic digestion, but one is considerably more economical to obtain than producing the other. The impact has been calculated for production of 1 m^3 of biogas from each feedstock.



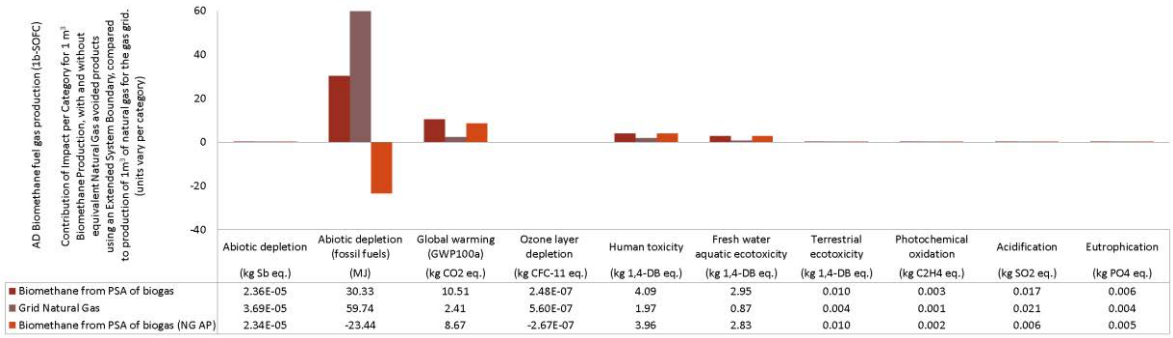
	Abiotic depletion (kg Sb eq.)	Abiotic depletion (fossil fuels) (MJ)	Global warming (GWP100a) (kg CO2 eq.)	Ozone layer depletion (ODP) (kg CFC-11 eq.)	Human toxicity (kg 1,4-DB eq.)	Fresh water aquatic ecotoxicity (kg 1,4-DB eq.)	Terrestrial ecotoxicity (kg 1,4-DB eq.)	Photochemical oxidation (kg C2H4 eq.)	Acidification (kg SO2 eq.)	Eutrophication (kg PO4 eq.)
Biogas from manure and biowaste by anaerobic digestion	2.06E-05	26.54	4.86	2.16E-07	3.58	2.58	0.01	0.001	0.01	0.005
Biogas from Miscanthus by anaerobic digestion	2.11E-05	27.35	4.93	2.32E-07	3.62	2.63	9.41E-03	0.001	0.01	0.01

Figure 5.17: Standard Characterisation impact assessment results for production of 1 m^3 biogas from biowastes and miscanthus energy crops (units dependent on impact category)

Due to energy crops being purpose grown for biofuels, the burdens of the inputs, agricultural processes, and harvesting are allocated to the energy crop feedstock. These burdens are then passed onto the biogas product. The benefits of using manure and biowastes over purpose grown energy crops are not substantial when compared side by side, as in *Figure 5.17*. Therefore, utilising resources from wastes is desirable from an environmental perspective. The economic and environmental benefits of not having to treat and dispose of the wastes are significant; considering the anaerobic digestor sludge and leftover digestate can be used as fertiliser substitutes and even feedstock for other biological processes like fermentation.

ii. Extended System Boundaries, and Avoided Products

Alternatively, there are also potential influences from extending the existing system boundaries so that they include avoided products that are now substituted with renewable product systems. There are discussions regarding biomethane from anaerobic digestion being supplied to the gas grid as a natural gas substitute, which would increase the concentrations of renewable gas in the grid. To assess the impact this would have, the equivalent avoided natural gas can be allocated to the biomethane system, which would provide insight to the potential environmental savings that could occur by using biomethane instead of natural gas (*Figure 5.18*).



	Abiotic depletion (kg Sb eq.)	Abiotic depletion (fossil fuels) (MJ)	Global warming (GWP100a) (kg CO2 eq.)	Ozone layer depletion (kg CFC-11 eq.)	Human toxicity (kg 1,4-DB eq.)	Fresh water aquatic ecotoxicity (kg 1,4-DB eq.)	Terrestrial ecotoxicity (kg 1,4-DB eq.)	Photochemical oxidation (kg C2H4 eq.)	Acidification (kg SO2 eq.)	Eutrophication (kg PO4 eq.)
Biomethane from PSA of biogas	2.36E-05	30.33	10.51	2.48E-07	4.09	2.95	0.010	0.003	0.017	0.006
Grid Natural Gas	3.69E-05	59.74	2.41	5.60E-07	1.97	0.87	0.004	0.001	0.021	0.004
Biomethane from PSA of biogas (NG AP)	2.34E-05	-23.44	8.67	-2.67E-07	3.96	2.83	0.010	0.002	0.006	0.005

Figure 5.18: Standard Characterisation impact assessment results for production of 1 m^3 biomethane from PSA of biogas from biowastes compared to 1 m^3 of grid natural gas and 1 m^3 of biomethane with avoided natural gas products (units dependent on impact category)

Figure 5.18 shows the impact of production 1 m^3 of biomethane from PSA of biogas compared to 1 m^3 of natural gas for the gas grid, in addition to 1 m^3 of biomethane from PSA of biogas with allocated avoided products (extended system boundary assessment) . The avoided products produce a negative impact bar, which demonstrates the amount of avoided emissions that would have been produced from the natural gas production system. The biomethane with avoided products allocated has a lower Abiotic Depletion (Fossil Fuels) environmental impact than both the standard biomethane system and the grid natural gas system, because a fossil resource is being replaced with a renewable one.

Regarding the rest of the impact categories, the grid natural gas system has a lower environmental impact because of the excessive quantities of gas being produced within that one system, compared to the small amounts of gas one energy intensive anaerobic digestor produces. This is a downside of assessing large scale and small scale systems. Ideally, both systems assessed need to be of similar sizes for results to show more comparable results. An example of this would be the allocation of palm cake from the palm oil waste stream to the soybean industry for animal feed products. Both systems are agricultural and would yield a similar amount of product, which would produce more comparable environmental impact results.

5.5.2. Metabolic Processing

Algal metabolic processing of biohydrogen has consistently performed well in the various assessments previously conducted, demonstrating its competitive potential. Like all biomass, algae sequestrate carbon dioxide as they grow. For this study in particular, the carbon dioxide pumped into the sealed photobioreactors has been harvested from a powerplant. Therefore, carbon dioxide inputs are assumed to be burden free, as all burdens are allocated to the power plant and its generated electricity [441]. Furthermore, if the

algal sludge (dead algal cells) that comes out of the photobioreactor is also collected, stored, and suitable for reuse in another pathway like anaerobic digestion or fermentation (or even for liquid fuel/biodiesel processes). This can result in carbon neutral emissions across more than one pathway [442, 443].

There are significant amounts of infrastructure and resources needed to build the photobioreactors, specifically the PMMA sheeting that covers the reactor to capture the gases and the liquid storage infrastructure, which is the largest impactor for a photobioreactor, with Abiotic Depletion (Fossil Fuels) and GWP^{100a} being the most affected impact categories. These are highlighted in *Figure 5.19* with high levels of fossil fuel use, which are intensively used in metal mining, manufacturing, and plastics like PMMA and HDPE.

Regarding improvements, there is research concerning growing algal biomass with agro-wastes, like slurries and wastewater [120, 121]. The agro-wastes have high carbon dioxide and nutrient contents, suspended in water, which is perfect for cultivating algae. Utilising this waste resource would significantly reduce the water, carbon dioxide, and nutrient demands of the photobioreactor system, as well as its environmental impact. In addition, swapping PVC and PMMA plastics for greener plastic substitutes could have advantages, though some are not yet commercially available [444].

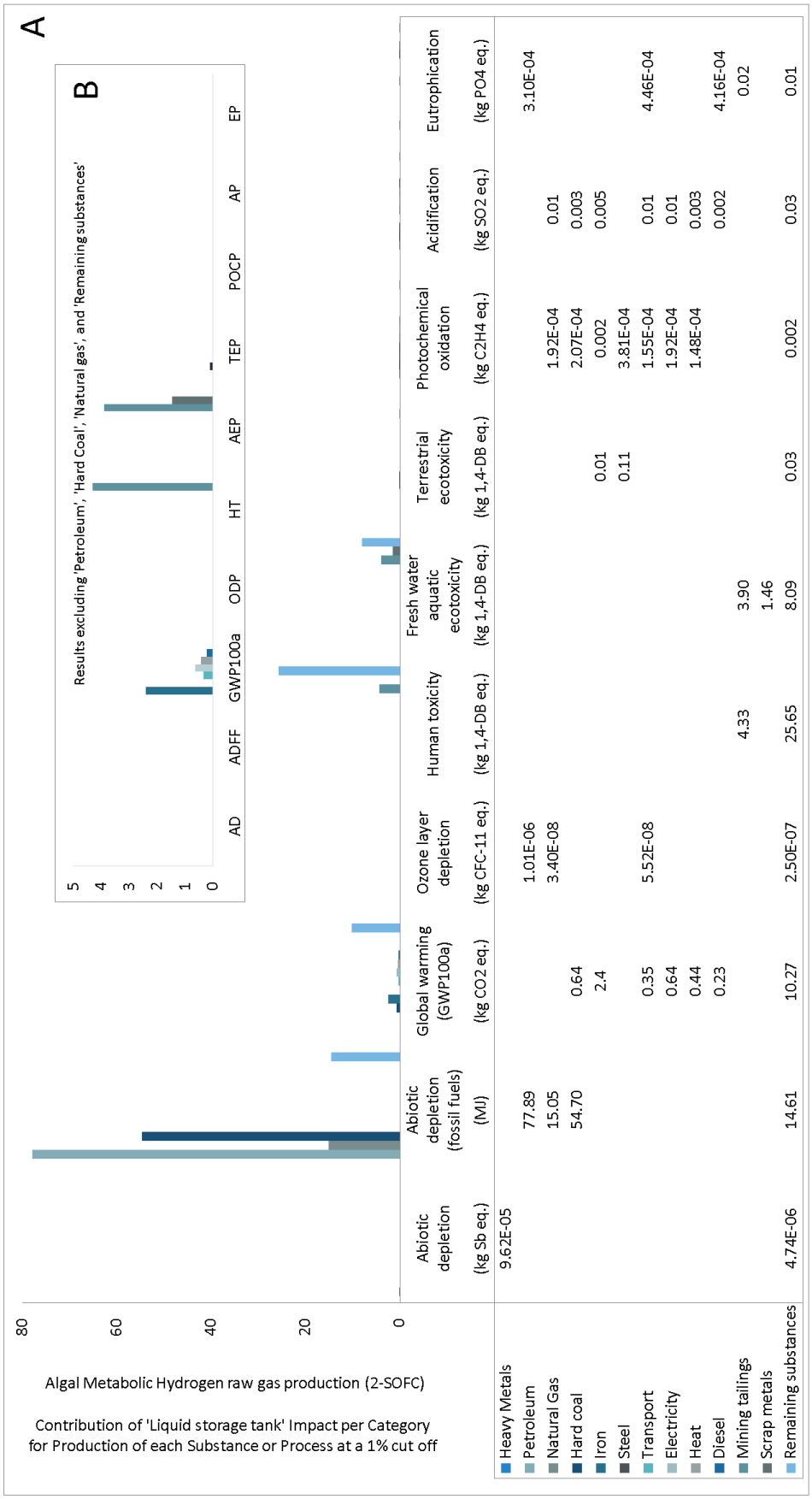
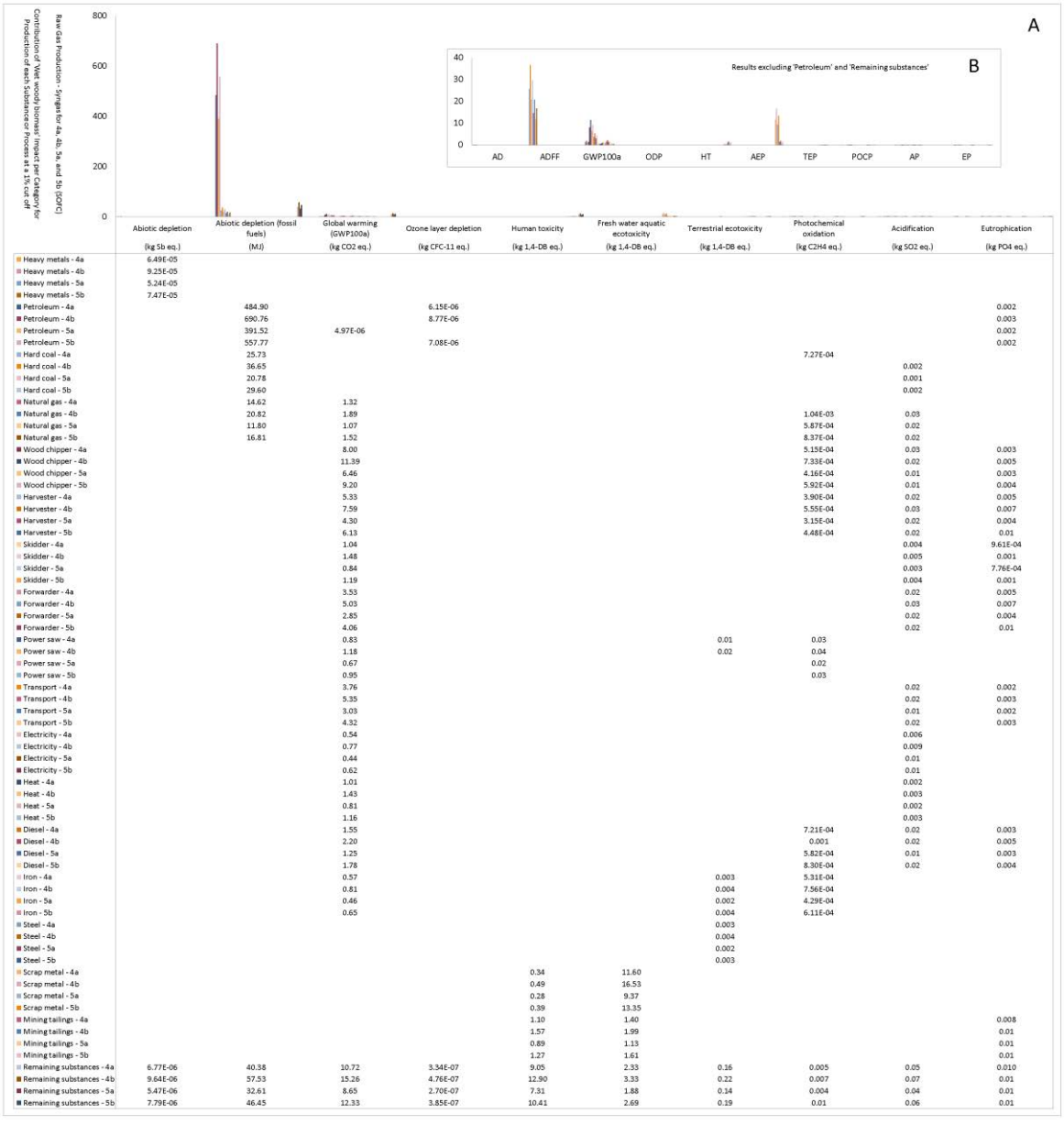


Figure 5.19: Substance contribution impact assessment results for 1 $MWh_{eq.}$ biohydrogen (2) for use in an SOFC (standard characterisation approach). A – whole system; B – whole system excluding 'Petroleum', 'Hard coal', 'Natural gas', and 'Remaining substances', to show smaller scale (units dependent on impact category)

5.5.3. Gasification and SCWG

The majorly affected impact categories from syngas produced by gasification (4a-SOFC) and SCWG (5a-SOFC), highlighted in the substance contribution assessment (*Figure 5.20)*, are Abiotic Depletion (Fossil Fuel), GWP^{100a}, Freshwater Aquatic Ecotoxicity Potential, and Human Toxicity; due to the procuring and processing of the wet woody biomass.

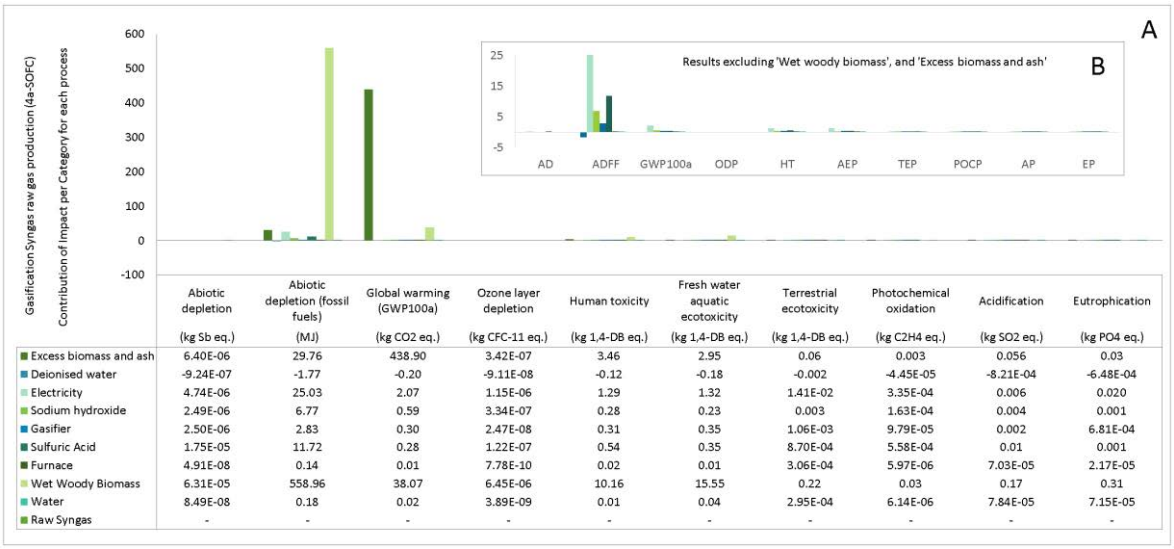


	Abiotic depletion (kg Sb eq.)	Abiotic depletion (fossil fuels) (MJ)	Global warming (GWP100a) (kg CO2 eq.)	Ozone layer depletion (kg CFC-11 eq.)	Human toxicity (kg 1,4-DB eq.)	Fresh water aquatic ecotoxicity (kg 1,4-DB eq.)	Terrestrial ecotoxicity (kg 1,4-DB eq.)	Photochemical oxidation (kg C2H4 eq.)	Acidification (kg SO2 eq.)	Eutrophication (kg PO4 eq.)
Heavy metals - 4a	6.49E-05									
Heavy metals - 4b	9.25E-05									
Heavy metals - 5a	5.24E-05									
Heavy metals - 5b	7.47E-05									
Petroleum - 4a		484.90		6.15E-06						0.002
Petroleum - 4b		690.76		8.77E-06						0.003
Petroleum - 5a		391.52	4.97E-06							0.002
Petroleum - 5b		557.77		7.08E-06						0.002
Hard coal - 4a		25.73						7.27E-04		
Hard coal - 4b		36.65							0.002	
Hard coal - 5a		20.78							0.001	
Hard coal - 5b		29.60							0.002	
Natural gas - 4a		14.62	1.32							
Natural gas - 4b		20.82	1.89					1.04E-03	0.03	
Natural gas - 5a		11.80	1.07					5.87E-04	0.02	
Natural gas - 5b		16.81	1.52					8.37E-04	0.02	
Wood chipper - 4a			8.00					5.15E-04	0.03	0.003
Wood chipper - 4b			11.39					7.33E-04	0.02	0.005
Wood chipper - 5a			6.46					4.16E-04	0.01	0.003
Wood chipper - 5b			9.20					5.92E-04	0.01	0.004
Harvester - 4a			5.33					3.90E-04	0.02	0.005
Harvester - 4b			7.59					5.55E-04	0.03	0.007
Harvester - 5a			4.30					3.15E-04	0.02	0.004
Harvester - 5b			6.13					4.48E-04	0.02	0.01
Skidder - 4a			1.04						0.004	9.61E-04
Skidder - 4b			1.48						0.005	0.001
Skidder - 5a			0.84						0.003	7.76E-04
Skidder - 5b			1.19						0.004	0.001
Forwarder - 4a			3.53						0.02	0.005
Forwarder - 4b			5.03						0.03	0.007
Forwarder - 5a			2.85						0.02	0.004
Forwarder - 5b			4.06						0.02	0.01
Power saw - 4a			0.83				0.01	0.03		
Power saw - 4b			1.18				0.02	0.04		
Power saw - 5a			0.67					0.02		
Power saw - 5b			0.95					0.03		
Transport - 4a			3.76						0.02	0.002
Transport - 4b			5.35						0.02	0.003
Transport - 5a			3.03						0.01	0.002
Transport - 5b			4.32						0.02	0.003
Electricity - 4a			0.54						0.006	
Electricity - 4b			0.77						0.009	
Electricity - 5a			0.44						0.01	
Electricity - 5b			0.62						0.01	
Heat - 4a			1.01						0.002	
Heat - 4b			1.43						0.003	
Heat - 5a			0.81						0.002	
Heat - 5b			1.16						0.003	
Diesel - 4a			1.55					7.21E-04	0.02	0.003
Diesel - 4b			2.20					0.001	0.02	0.005
Diesel - 5a			1.25					5.82E-04	0.01	0.003
Diesel - 5b			1.78					8.30E-04	0.02	0.004
Iron - 4a			0.57				0.003	5.31E-04		
Iron - 4b			0.81				0.004	7.56E-04		
Iron - 5a			0.46				0.002	4.29E-04		
Iron - 5b			0.65				0.004	6.11E-04		
Steel - 4a							0.003			
Steel - 4b							0.004			
Steel - 5a							0.002			
Steel - 5b							0.003			
Scrap metal - 4a					0.34	11.60				
Scrap metal - 4b					0.49	16.53				
Scrap metal - 5a					0.28	9.37				
Scrap metal - 5b					0.39	13.35				
Mining tailings - 4a					1.10	1.40				0.008
Mining tailings - 4b					1.57	1.99				0.01
Mining tailings - 5a					0.89	1.13				0.01
Mining tailings - 5b					1.27	1.61				0.01
Remaining substances - 4a	6.77E-06	40.38	10.72	3.34E-07	9.05	2.33	0.16	0.005	0.05	0.010
Remaining substances - 4b	9.64E-06	57.53	15.26	4.76E-07	12.90	3.33	0.22	0.007	0.07	0.01
Remaining substances - 5a	5.47E-06	32.61	8.65	2.70E-07	7.31	1.88	0.14	0.004	0.04	0.01
Remaining substances - 5b	7.79E-06	46.45	12.33	3.85E-07	10.41	2.69	0.19	0.01	0.06	0.01

Figure 5.20: Substance contribution impact assessment results for 1 $MWh_{eq.}$ syngas for 4a and 5a for use in an SOFC – A – whole system; B – whole system excluding 'Petroleum' and 'Remaining substances', to show smaller scales (units dependent on impact category)

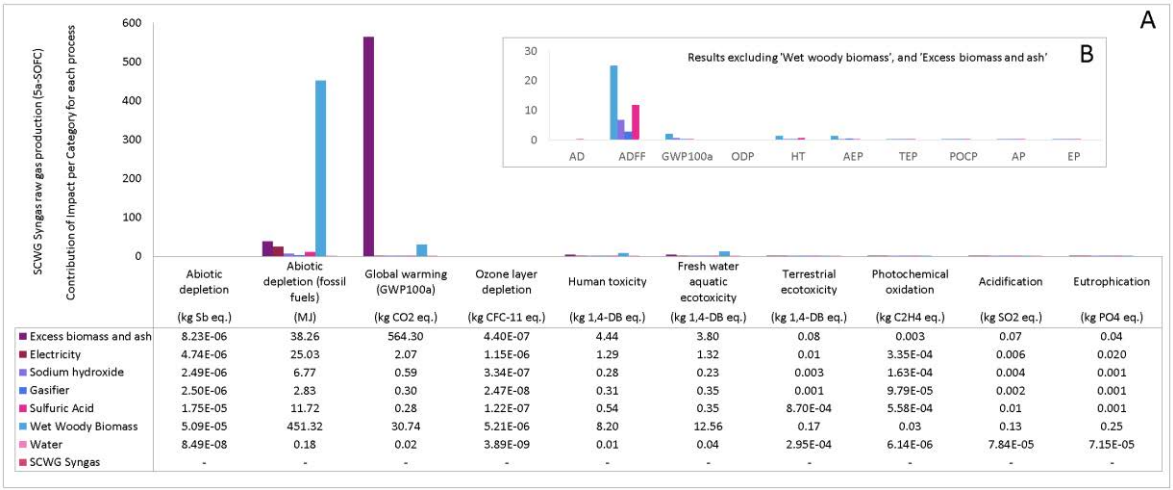
The biomass feedstock is not completely consumed in the SCWG process, as it is only ~70% efficient compared to gasification's ~75%. In addition, the water removed from woody biomass for gasification, as the biomass must have a moisture content <10%, can be sold to industry as pure distilled water (*as shown in the avoided product results of Figure 5.20*). This is because gasification has an extra 'furnace' subprocess, as it requires dry biomass to produce raw syngas due to the conditions within the gasifier.

On the other hand, SCWG utilises wet biomass and uses the feedstock as received as no additional drying processes required. The drying process, however, does increase the LHV of biomass feedstocks, but more feedstock is required to feed this demand [68]. Conversely, the 'wet woody biomass' waste residues and 'excess biomass and ash' impacts are substantially higher than other areas of the system. The 'excess biomass and ash' are produced from a not 100% efficiency gasification process (*Figures 5.21 and 5.22*). The 'wet woody biomass' impacts predominately driven by the logging processes for harvesting, gathering, processing, and transporting the wood residue wastes, along with the production of this infrastructure (as seen in *Figure 5.20*).



	Abiotic depletion (kg Sb eq.)	Abiotic depletion (fossil fuels) (MJ)	Global warming (GWP100a) (kg CO2 eq.)	Ozone layer depletion (kg CFC-11 eq.)	Human toxicity (kg 1,4-DB eq.)	Fresh water aquatic ecotoxicity (kg 1,4-DB eq.)	Terrestrial ecotoxicity (kg 1,4-DB eq.)	Photochemical oxidation (kg C2H4 eq.)	Acidification (kg SO2 eq.)	Eutrophication (kg PO4 eq.)
Excess biomass and ash	6.40E-06	29.76	438.90	3.42E-07	3.46	2.95	0.06	0.003	0.056	0.03
Deionised water	-9.24E-07	-1.77	-0.20	-9.11E-08	-0.12	-0.18	-0.002	-4.45E-05	-8.21E-04	-6.48E-04
Electricity	4.74E-06	25.03	2.07	1.15E-06	1.29	1.32	1.41E-02	3.35E-04	0.006	0.020
Sodium hydroxide	2.49E-06	6.77	0.59	3.34E-07	0.28	0.23	0.003	1.63E-04	0.004	0.001
Gasifier	2.50E-06	2.83	0.30	2.47E-08	0.31	0.35	1.06E-03	9.79E-05	0.002	6.81E-04
Sulfuric Acid	1.75E-05	11.72	0.28	1.22E-07	0.54	0.35	8.70E-04	5.58E-04	0.01	0.001
Furnace	4.91E-08	0.14	0.01	7.78E-10	0.02	0.01	3.06E-04	5.97E-06	7.03E-05	2.17E-05
Wet Woody Biomass	6.31E-05	558.96	38.07	6.45E-06	10.16	15.55	0.22	0.03	0.17	0.31
Water	8.49E-08	0.18	0.02	3.89E-09	0.01	0.04	2.95E-04	6.14E-06	7.84E-05	7.15E-05
Raw Syngas	-	-	-	-	-	-	-	-	-	-

Figure 5.21: Standard Characterised impact assessment results of production 1 $MWh_{eq.}$ of Raw Syngas from Gasification, with 'Deionised water' avoided products. A – Whole system; B – whole system excluding: 'Wet woody biomass', and 'Excess biomass and ash' (units dependent on impact category)



	Abiotic depletion (kg Sb eq.)	Abiotic depletion (fossil fuels) (MJ)	Global warming (GWP100a) (kg CO2 eq.)	Ozone layer depletion (kg CFC-11 eq.)	Human toxicity (kg 1,4-DB eq.)	Fresh water aquatic ecotoxicity (kg 1,4-DB eq.)	Terrestrial ecotoxicity (kg 1,4-DB eq.)	Photochemical oxidation (kg C2H4 eq.)	Acidification (kg SO2 eq.)	Eutrophication (kg PO4 eq.)
Excess biomass and ash	8.23E-06	38.26	564.30	4.40E-07	4.44	3.80	0.08	0.003	0.07	0.04
Electricity	4.74E-06	25.03	2.07	1.15E-06	1.29	1.32	0.01	3.35E-04	0.006	0.020
Sodium hydroxide	2.49E-06	6.77	0.59	3.34E-07	0.28	0.23	0.003	1.63E-04	0.004	0.001
Gasifier	2.50E-06	2.83	0.30	2.47E-08	0.31	0.35	0.001	9.79E-05	0.002	0.001
Sulfuric Acid	1.75E-05	11.72	0.28	1.22E-07	0.54	0.35	8.70E-04	5.58E-04	0.01	0.001
Wet Woody Biomass	5.09E-05	451.32	30.74	5.21E-06	8.20	12.56	0.17	0.03	0.13	0.25
Water	8.49E-08	0.18	0.02	3.89E-09	0.01	0.04	2.95E-04	6.14E-06	7.84E-05	7.15E-05
SCWG Syngas	-	-	-	-	-	-	-	-	-	-

Figure 5.22: Standard Characterised impact assessment results of production 1 $MWh_{eq.}$ of Raw Syngas from SCWG. A – Whole system; B – whole system excluding: 'Wet woody biomass', and 'Excess biomass and ash' (units dependent on impact category)

In addition, the syngas fuel gas output impacts themselves, which are made up of biogenic carbon dioxide, are another contributor. However, these are considered as neutral carbon, due to carbon dioxide sequestration during biomass growth [445]. There are emissions of fossil carbon dioxide and Human Toxicity impact from the use and extraction of heavy metals, heavy coal, natural gas, and oil for the resources and energy needed to build and run the gasifier.

Regarding the net carbon dioxide emissions only, the amount of fossil carbon dioxide emitted from post syngas production processes (gas clean-up and SOFC internal reforming/hydrogen reforming) is negated due to biogenic carbon, as it originates from the atmosphere and being taken up by biomass for growth. If this biogenic carbon dioxide was capture and stored, preventing its return to the atmosphere, each raw syngas system would negate the following amounts of carbon dioxide per $MWh_{eq.}$ of produced raw syngas: 4a - 396.48 kg, 4b - 564.81 kg, 5a - 532.51 kg, and 5b - 758.40 kg. However, all carbon dioxide emissions from the wet woody biomass hot spot identified in this impact assessment are from fossil fuel derived machines and processes outside of the biological carbon cycle.

5.5.4. Fossil Fuel Reference Cases

The final contribution analysed is that of the fossil reference case systems, for completeness. The raw natural gas from the reserve (gas well) has the highest impact, as anticipated, influencing GWP^{100a} impacts. This subprocess has significant fossil natural gas resource depletion substance contributions (*Figure 5.23, part A*), which have been excluded in *Figure 5.23, part B* (alongside mining tailings and the remaining negligible 1% substances) so the contributions of sulfur dioxide and nitrogen oxides can be seen, which is important as they both affects the Human Toxicity and Acidification Potential impact categories. These impacts would be reduced if removed contaminant gases were captured and not released into the atmosphere.

Unlike the biomass pathways, the highest impact contributor for the fossil fuel reference cases is not a subprocess system for clean-up, but the raw natural gas itself, within the gas well. Therefore, where the biological pathways have alternative methods and technologies for their reforming/clean-up, and can potentially reduce their environmental impact, natural gas cannot as its extraction is an unavoidable process. However, the natural gas powering the processing plant can be replaced with alternative energy generation (renewable energy, geothermal, or even potentially a fuel cell running off any of the fuels explored in this assessment) to reduce additional environmental impacts [228, 268, 446].

There have also been studies on the potential for rigging molten carbonate fuel cells up to power plant exhausts in a combined cycle and running the fuel cells on methane produced from the exhaust carbon dioxide; clean-up processes would not be necessary as they are not susceptible to poisoning [156, 267, 269].

	Abiotic depletion (kg Sb eq.)	Abiotic depletion (fossil fuels) (MJ)	Global warming (GWP100a) (kg CO2 eq.)	Ozone layer depletion (ODP) (kg CFC-11 eq.)	Human toxicity (kg 1,4-DB eq.)	Fresh water aquatic ecotoxicity (kg 1,4-DB eq.)	Terrestrial ecotoxicity (kg 1,4-DB eq.)	Photochemical oxidation (kg C2H4 eq.)	Acidification (kg SO2 eq.)	Eutrophication (kg PO4 eq.)
Heavy metals - RCa	4.28E-05				2.96	0.80	0.01	0.03	0.43	0.002
Heavy metals - RCb	3.75E-05				2.60	0.70	0.01	0.02	0.37	0.002
Natural gas - RCa		9,904.88	27.26		2.21		0.02	0.01	0.19	0.01
Natural gas - RCb		8,689.95	23.92		1.94		0.02	0.01	0.17	0.01
Electricity - RCa			34.61							
Electricity - RCb			30.37	9.95E-05						
Transport - RCa			29.23	8.73E-05				0.01		
Transport - RCb			25.64					0.01		
Hard coal - RCa			1.27							
Hard coal - RCb			1.12							
Mining tailings - RCa					8.27	14.36	0.01			0.09
Mining tailings - RCb					7.26	12.60	0.01			0.08
Scrap metals - RCa						2.25				
Scrap metals - RCb						1.97				
Steel - RCa							0.02			
Steel - RCb							0.02	0.001		
Iron - RCa							0.003	0.001		
Iron - RCb							0.003		0.01	0.003
Diesel - RCa									0.01	0.003
Diesel - RCb										
Remaining substances - RCa	3.10E-06	720.43	33.22	4.67E-06	11.98	6.58	0.09	0.01	0.12	0.06
Remaining substances - RCb	2.72E-06	632.06	29.14	4.09E-06	10.51	5.78	0.08	0.01	0.11	0.05

Figure 5.23: Subprocesses, inputs, and outputs contribution impact assessment results for 1 $MWh_{eq.}$ of raw natural gas for both fossil fuel reference cases (RCa and RCb) for use in an SOFC. A – whole system; B – whole system excluding 'Natural gas', 'Mining tailings', and 'Remaining substances', to show smaller scales (units dependent on impact category)

5.6. Fuel Cells vs Renewable Technologies

It has been previously observed that gaseous fuels from both biomass with similar compositions to fossil fuel gases, *i.e*. high methane content, are suitable substitutes for fossil fuels for use in fuel cells. There has also been mention of renewable technologies for onsite energy generation, but fuel cells are also suitable for large-scale stationary power generation. *Figure 5.24* demonstrates the competitivity of SOFCs and PEFCs when compared to wind and solar renewable technologies, utilising a 1 MWh electrical output functional unit. The fuel cells are both running on biohydrogen from algal metabolic processing, as it was the lowest impacting fuel gas for both SOFC and PEFC systems in the previous assessment.

The legend is ordered from least to most environmentally impactful, with both the renewable technologies close together towards the centre and the fuel cells, whose results are also close together, being further out towards the edge. Despite the two fuel cells running on the same gas, SOFCs continue to demonstrate their advantage over PEFCs. These are the normalised results from characterised data, with logarithmic scaling, which allow clear comparison of each electrical system and their driving environmental impact categories.

The predominate influencers for the renewable technologies are the heavy demands on metals, such as steel and copper, and their extensive scrap wastage. The PEFC is driven by platinum, waste plastic, and phenolic resin. Comparatively, the SOFCs impacts are predominately determined by lanthanum oxide. It is the production of these substances and their unutilised scrappage wastes that results in these impacts, and therefore if procedures were in place, within industry, for recycling the scraps into reusable products, environmental impacts would be minimised.

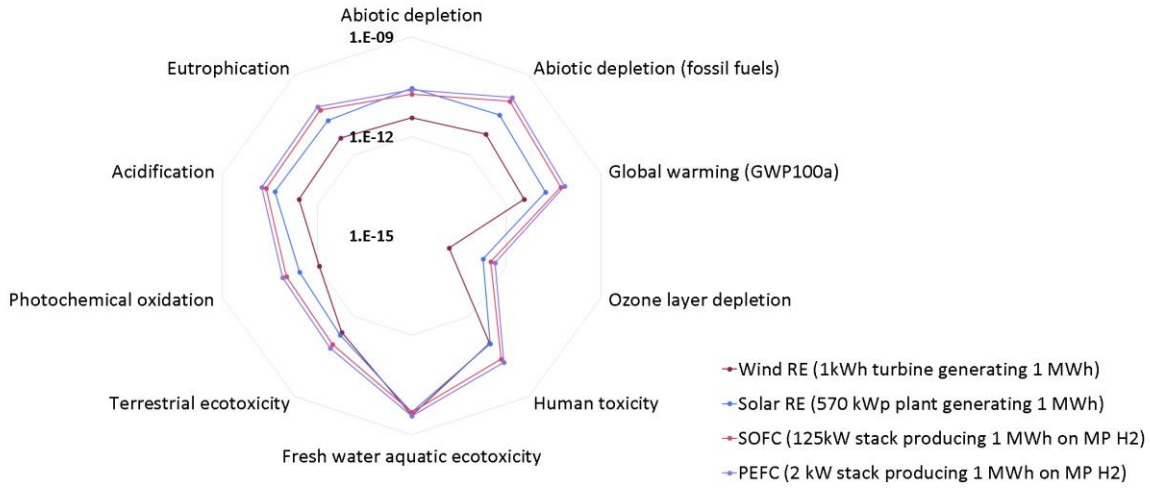


Figure 5.24: Normalised comparative impact assessment of 1 $MWh_{eq.}$ electrical output from: two fuel cell stacks running on biohydrogen (125 kW SOFC and 2 kW PEFC stacks) and renewable energy technologies (570 kWp Solar plant and 1 kWh Wind turbine).

5.7. Key Findings

Across this assessment, subsystem boundaries within the same overriding system have been analysed for their environmental impact contribution. The degrees of impact have changed within each system boundary, and therefore a final ranking must be made for the true lowest and highest impactors to be identified.

Due to the number of impact categories, it is not possible to provide one emission unit for each pathway, without weighting, and utilising data normalisation has provided a deeper level of analysis to the LCA results. Therefore, a clearly numbered ranking system was introduced so that the overall lowest (1) and highest (15) impact contributors for each system boundary assessed is distinct, as well as a definitive total across all assessment areas. All of the fuel gas systems have data that has undergone both characterisation and normalisation analysis, which have been compiled into a single ranking to allow both perspectives to have influence on the final rankings. *Table 5.5* summarises and ranks all the

fuel gas pathways assessed, including the raw biomass and fuel gas demands for the fermentation pathways, which were excluded from the LCA.

Table 5.5: Systematic review and LCA results for all LCA assessed pathways, with four additional biomass pathways

Fuel Gas Demand, Raw Gas Demand, and Raw Feedstock Demand unmodified data source: [68]

Ref.	Fuel Gas	Fuel Gas Demand (kg/MWh)	Raw Gas Demand (kg/MWh)	Raw Feedstock Demand (kg/MWh)	A: Feedstock Demand Ranking (1 = lowest, 19 = highest)	B: LCA Raw Gas Impact Ranking (1 = lowest, 15 = highest)	C: LCA Fuel Gas Impact Ranking (1 = lowest, 15 = highest)	D: LCA Whole System Impact Ranking (1 = lowest, 15 = highest)	Total Ranking (A+B+C+D)	Final Ranking
2-SOFC	Biohydrogen	49.99	58.81	858.62	6	3	1	1	11	1
4a-SOFC	Syngas	461.50	727.57	863.82	7	1	2	3	13	2
5a-SOFC	Syngas	461.50	545.67	697.48	5	2	3	4	14	3
2-PEFC	Biohydrogen	66.66	78.43	1,144.94	10	7	4	2	23	4
5b-SOFC	Hydrogen (SG)	49.99	691.95	988.50	8	6	6	6	26	5
4b-SOFC	Hydrogen (SG)	49.99	922.56	1,224.20	11	5	5	5	26	6
1c-SOFC	Hydrogen (BM)	49.99	162.79	217.05	1	9	10	10	30	7
1b-SOFC	Biomethane	119.99	166.08	221.44	2	10	9	9	30	8
4b-PEFC	Hydrogen (SG)	66.66	922.69	1,624.34	14	4	7	7	32	9
5b-PEFC	Hydrogen (SG)	66.66	922.60	1,318.00	12	8	8	8	36	10
1a-SOFC	Biogas	166.65	199.99	236.18	3	11	11	11	36	11
1c-PEFC	Hydrogen (BM)	66.66	217.09	289.45	4	12	13	13	42	12
RCb-SOFC	*(Fossil) Hydrogen*	*49.99*	*145.66 **	*n/a*	*17*	*15*	*15*	*12*	59	*13*
RCb-PEFC	*(Fossil) Hydrogen*	*66.66*	*194.24 **	*n/a*	*19*	*13*	*12*	*15*	59	*14*
RCa-SOFC	*De-sulphured Natural Gas*	*157.98*	*166.30 **	*n/a*	*18*	*14*	*14*	*14*	60	15
3a-SOFC	Hydrogen	49.99	58.81	1,131.52	9	n/a	n/a	n/a	n/a	16
3a-PEFC	Hydrogen	66.66	78.43	1,508.88	13	n/a	n/a	n/a	n/a	17
3b-SOFC	Hydrogen	49.99	58.81	1,851.58	15	n/a	n/a	n/a	n/a	18
3b-PEFC	Hydrogen	66.66	78.43	2,469.07	16	n/a	n/a	n/a	n/a	19

** Sour Natural Gas, extracted from gas well*

Reference guide:

1a Anaerobic Digestion, Biogas
1b Anaerobic Digestion, Biomethane from Biogas
1c Anaerobic Digestion, Hydrogen from Biomethane
2 Metabolic Processing, Hydrogen
3a Dark Fermentation, Hydrogen
3b Light Fermentation, Hydrogen
4a Gasification, Syngas
4b Gasification, Hydrogen from Syngas
5a Supercritical Water Gasification, Syngas
5b Supercritical Water Gasification, Hydrogen from Syngas
RCa Reference Case, Natural Gas
RCb Reference Case, Hydrogen from Natural Gas

Column A allocates a ranked order for the raw biomass feedstock demand, which was calculated using the raw gas demand and the efficiencies of the gas processing techniques used to produce the required fuel gas demand. *Columns B to D* are based on the EU25 normalised data results in *Sections 5.4.2, 5.4.3, and 5.4.4,* ranking the orders of*:* raw fuel gas analyses, fuel gas, and whole system analyses, respectively:

- The fossil reference cases (RCa-SOFC, RCb-SOFC, and RCb-PEFC) were found to have the greatest impacts of the assessed systems, ranking 13th, 14th, and 15th, respectively.
- The four anaerobic digestion systems have intermediate rankings (1c-SOFC – 7th, 1b-SOFC – 8th, 1a-SOFC – 11th, and 1c-PEFC – 12th, respectively).
- The hydrogen from syngas systems ranked at 5th (5b-SOFC) and 6th (4b-SOFC), as well as 9th (4b-PEFC) and 10th (5b-PEFC)which highlights potential substitute for fossil derived hydrogen.
- Syngas from gasification (4a-SOFC) and SCWG (5a-SOFC) are ranked 2nd and 3rd, respectively, with Biohydrogen (2-SOFC) at the top of the rankings (1st) with 2-PEFC ranking 4th; also demonstrating that algae have competitive potential for fuel gases, in addition to their established biodiesel applications.

Chapter 5's initial findings from the previous work on raw feedstock and fuel gas demands [68] also demonstrate the importance of assessing more than one perspective. However, biohydrogen (2-SOFC) and syngas (4a-SOFC and 5a-SOFC) ranked consistently well compared to other systems, such as the anaerobic digestion systems (1a, 1b, and 1c), which broadly ranked lower with their high environmental impact for the raw feedstock, whole system, and fuel gas assessments.

Regarding the fuel cells, SOFCs continue to stand out thanks to their high efficiencies and robust fuel gas choices, but 2-PEFC performed particularly well compared to the other PEFC systems (4th , compared to the next PEFC system (1c-PEFC), which is ranked 9th).

5.8. Assessment Conclusions

With the depletion of fossil fuels, alternative sources of fuel gases must be found, whilst also improving their environmental impact and ensuring resource sustainability. By utilising biomass, fuel gases can be sourced from several feedstocks, including biowastes; which performed better than purpose grown energy crops. This assessment has continued from a systematic review that identified typical raw feedstock demands and their respective fuel gas demand for using biomass derived fuels in fuel cell technologies. The competitive nature of biohydrogen, syngas, and biomethane were identified and found to be viable alternatives to fossil fuel reference cases, which were ranked below them, as well as hydrogen from syngas technologies being additional suitable substitutes for hydrogen made from steam reformed natural gas (RCb-SOFC, and RCb-PEFC - current commercial method).

Of the fuel cell technologies assessed, SOFC systems were found to be both some of the lowest and highest contributors to environmental impacts, dependant on the fuel gases used. This is because the production of the fuel gases dominated the environmental impact of the whole fuel cell system boundary (*Figure 5.6*). PEFC systems were found to have a variety of impact performances - also dependant on methods the hydrogen was produced with. With advancements in biomass conversion processes and their technologies, the dominating impacts of large scale industrial processes could be reduced and bring forth a new era of cleaner, greener, sustainable gaseous fuels.

CHAPTER 6

CHAPTER 6. CONCLUSIONS AND FUTURE WORK

With the increasing demand for sustainable, cleaner sources of energy and advancements towards carbon neutral technologies, international environmental legislation requires supporting evidence and research from the scientific community. Advancements in implementation of governmental policies seeks to encourage the deployment of renewable technologies, as well as guidance and regulations on conventional fossil fuel power plants to decrease their carbon emissions. The need for decarbonising the energy sector is increasing, especially with recent environmental summits, and a vast consensus amongst climate scientists that climatic changes are accelerating and increasing in intensity (more destructive hurricane seasons, extended periods of droughts and flooding).

6.1. Research Conclusions

The purpose of this research was to identify alternative sources and methods of obtaining gaseous fuels for fuel cells from biomass and biowastes. An investigation of their environmental impact, in comparison to fossil fuel reference cases, was also required in order to determine their competitivity and viability. The chosen methodology was Life Cycle Analysis (LCA), with use of LCA software, biomass to gas data calculated in this thesis, and database data for standard processes and technologies so robust, encompassing results could be produced. In order to achieve this purpose, a number of aims and objectives were set and have been methodically approached and accomplished throughout this thesis; albeit not chronologically (outlined in *Chapter 1, Table 1.1*). This research resulted in the identification of several fuel gas pathways that were environmental competitive to the fossil fuel reference cases.

6.1.1. Understanding LCA

In order to properly conduct an LCA, a Palm Oil Biodiesel case study was utilised for the exploration of different LCA methodologies and helped to gain a new understanding of the varieties of techniques available. The guidance provided by the ISO standards (ISO 14040 and 14044) established a core four-stage method that all LCA practitioners must abide by to be consistent, with ISO 14025 providing in-depth guidance for comparative LCAs (i.e. using the same assessment parameters, system boundaries, plant operating lifetime, functional unit, impact categories, impact assessment methodology, *etc.*). This case study found that most LCA practitioners and researchers conduct studies differently, resulting in different results that make comparative studies difficult without significant data modifications.

A generic life cycle inventory, unique to this field, was produced, alongside a comparative assessment of different types of data units (mass quantity (kg), energy content equivalence ($MJ_{eq.}$), and carbon equivalent (kg $CO_{2eq.}$). This assessment found that depending which unit was used, the results changed and each unit had little resemblance to the others. This highlighted the importance of always using a mass based inventory, as well as an additional unit, within any assessment for accurate and transparent results. The methodological findings from this case study were applied to this research.

In addition, an in-depth analysis of the data set formed from published LCA inventories found that geography, and the individual data collection and LCA methods used influenced their results significantly. For instance, when investigating the fresh fruit bunch (FFB) composition, including wastes and products, from each study they all had variations in the FFB masses; something that should theoretically be the same, or within a 3% error tolerance.

6.1.2. Biomass Derived Fuels

Concerning advancements in biomass conversion techniques, the three core biomass generations were discussed (first, second and third generation biomass – energy crops, wood waste residues and biowastes, and algae, respectfully). Several biomass conversion pathways were identified from literature – anaerobic digestion, metabolic processing, (light and dark) fermentation, gasification, supercritical water gasification (SCWG). These pathways can produce a multitude of gaseous and liquid fuel products from a variety of waste biomass feedstocks.

For use of these fuels, an overview of different types of fuel cells, a technology that converts a fuel gas (e.g. hydrogen) to electricity electrochemically was presented. It was decided the best technology choices for this assessment were Solid Oxide Fuel Cell (SOFC) and Polymer Exchange Fuel Cell (PEFC) because they represented fuel cells of different temperature types (high *versus* low), and had different compatible fuels (natural gas, pure methane, syngas, and pure hydrogen *versus* only pure hydrogen). The functional unit for this research was specified as 1 MWh of electrical fuel cell output (1 $MWh^{elec.}$).

A novel synthesis of experimental data for gaseous fuels from biomass was produced. This was calculated from first principals, alongside process efficiencies and gas clean-up technologies was successfully derived. All gaseous biomass pathways identified were established alongside fossil derived reference cases. Various types of data were calculated in a mass balance for the production of the 1 $MWh^{elec.}$ functional unit:

A) Fuel Gas Demand – the amount of useable fuel gas that the fuel cells required to produce 1$MWh^{elec.}$ (*e.g.* cleaned-up syngas or pure hydrogen).

B) Raw Gas Demand – the amount of raw gaseous fuel required to produce 1 $MWh^{elec.}$ Equivalent of Fuel Gas (A) after clean-up/reforming (*e.g.* raw syngas).

C) Raw Feedstock Demand – the amount of raw biowastes* required to produce the demanded Raw Fuel Gas (B) (*e.g.* waste wood residues).

**The fossil reference cases were excluded from (C) due to not coming from biological sources.*

This data was ranked in order of lowest to highest Raw Feedstock Demand because some pathways that produced the lowest Fuel Gas Demands required well over 1 tonne of biomass wastes to produce the same output as all the other systems (Fermentation being one of them). Anaerobic digestion was found to be the best pathway across both SOFC and PEFC systems, for all three of its fuel gases: biogas, biomethane, and hydrogen. This data was utilised as production inventory data (inputs, processes, and outputs) for the comparative LCA.

6.1.3. Comparative LCA

Finally, the conduction of a comparative LCA of viable biomass pathways produced a multitude of results, across three impact assessments:

A) Processing of Raw Feedstock for equivalent Raw Gas Demand

B) Clean-up/Reforming of Raw Gas into a useable Fuel Gas, equivalent to $1MWh^{elec.}$

C) Whole fuel cell system, producing $1MWh^{elec.}$ on the demanded Fuel Gas

An assessment such as this has not been produced before for this number of biomass pathways, providing novelty within this field. This research found that fuel gas systems that

require many processes tend to have more losses than simpler systems, due to losses in every process step. Therefore, more raw gas was required to mitigate these losses. This also drove the Raw Feedstock Demand, as greater quantities of raw gas require more resources. All impacts found here were for the production of the fuel gases themselves, with much impact contribution coming from the production of the infrastructure needed to process the biowastes.

This research has provided insight that even pathways with low efficiency and high fuel gas demands have the potential for low ecological impacts, as metabolic processing has some of the lowest process efficiencies due to biological limitations, whilst also producing high yields of gas per kg of biomass feedstock (in this case, algae). Fuels derived from biomass were found to be highly ecologically competitive against fossil fuel reference cases, with third generation algal metabolic processing pathways and second generation biowastes utilised in SCWG, being the most favourable, followed by anaerobic digestion. SOFCs also proved to be a more favourable technology than PEFCs, due to their wide range of fuel choices and higher efficiency.

6.2. Key Take-Home Messages

6.2.1. Implications of Key Findings and Recommendations

Through the exploration of LCA methodologies, it is important to understand the varieties of techniques available (*A.1*), the guidance provided by the ISO standards (ISO 14040 and 14044) have established a core four-stage rule that all LCA practitioners must abide by to be consistent. ISO 14025 also provides in-depth guidance for comparative LCAs. However, the issues of non-legally binding regulations regarding the methods of conducting and reporting an LCA lead to deviations in erratic study results, for seemingly the same topics. Drivers of such inconsistencies include: variations in the system boundaries (whole or

partial system analysis); functional units (quantity, energy, or carbon equivalence); transparency of data collection techniques (primary and/or secondary data, included and excluded data fields); lifetime of the system; and the geography of each study. Maintaining this balance is critical for comparative studies, in addition to clear, transparent reporting.

Regarding advancements in biomass conversion techniques, three core biomass generations have been found to provide a multitude of gaseous and liquid fuel products from a variety of feedstocks (energy crops, biowastes, *etc*.) (*A.2*). There is extensive research on liquid fuels from biomass, but fewer studies for gaseous fuels, comparative studies, and even fewer with LCA. Implications of such advancements are the potential surge in waste reuse, and the practicality and costs of such an operation. The human population produces around 1.3 billion tonnes of waste each year, some countries even shipping their wastes internationally to be processed. Therefore, a reduction in waste and alternative uses for non-recyclable items is imperative.

There is also the influence that substitute products have on another primary market. For instance, palm oil decanter cake (by-product waste of the crude palm oil extraction process) can be sold on the animal feed market as an alternative to soybeans. Therefore, if palm oil decanter cake was sold, this would have implications on the soybeans they are replacing. The food vs energy debate is a dominant topic in this field, but requires in-depth, standalone research of its own to do it justice.

Finally, the conduction of a comparative LCA of viable biomass pathways (*A.3*) produced a multitude of results, across a number of assessments. Fuels derived from biomass were found to be highly ecologically competitive against fossil fuel reference cases, with 3rd generation algal pathways and 2nd generation biowastes utilised in anaerobic digestion, being the most favourable, followed by SCWG. The benefits of algal metabolic processing

are the production of biohydrogen fuel gas, whilst also providing oil rich algal biomass for utilisation in the liquid fuel market.

Pyrolysis and hydrothermal liquefaction were two biomass conversion methods not included in this assessment, due to their core products being liquid fuels and bio-char. However, the wastes and by-products from producing gaseous fuels can also be utilised in these thermochemical pathways for liquid fuels, thus increasing the number of products available from one resource. In addition, the gaseous products from anaerobic digestion, primarily biogas and biomethane, can be injected into the national gas grid as a natural gas substitute. These would therefore be able to reduce demand for imported natural gas, as well as providing heat and power to domestic communities.

6.3. Research and Data Limitations

As with all data, there are issues of consistently keeping things up to date. Consequently, there are many potential issues caused by updating incomplete data sets and models to a newer version: broken links and data set corruption. This can result in pre-existing models no longer functioning and either having to be remade using the newer versions of the database or rolled back to the previous version they were created with. However, so long as all data sets across all assessed systems are consistent in the database version used, properly documented, and contain the same level of detail, the results will be more accurate than those using mixed database versions. In cases where some results were not expected (e.g. biowastes vs energy crops for biogas production) LCA software can inhibit the user from exploring drivers more deeply, as unless you manually created every data set from your own primary data, it is not possible to identify exactly what has been allocated to and from where. Therefore, further exploration into alternative LCA methods is advised.

6.4. Further Work

The research in this thesis is theoretical and would benefit from practical lab experiments to test and compare the findings to those of an industrial/pilot plant. The collection of primary data, as opposed to relying on secondary and database data, would be valuable further work to take this research to the next level. This could be tailored into a techno-economic analysis, which would also allow an economic assessment of the costs of each gaseous fuel produced, so they can be ranked against cost effectiveness as well as environmental impact. For instance, algal metabolic hydrogen production data in the 2009 NREL techno-economic analysis report [63] calculated the hydrogen gas product cost from \$2.99 kg^{-1} to \$8.15 kg^{-1} hydrogen (range specified at near term performance and upper bound performance). For comparison, the commercial average for hydrogen produced from natural gas was around \$4.50 kg^{-1} hydrogen in 2011 [447].

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APPENDICES

APPENDIX A. ATTACHED THESIS DISK

A.1. : Biomass to Gas Data and Mass Balance Spreadsheets

Please see this folder for the excel spreadsheet covering how all key inventory data was calculated, from first principals.

A.2. : Biomass to Gas LCA Impact Assessment Results

Please see this folder for all SimaPro LCA impact results, which were produced from the key inventory data and process data from the EcoInvent 3.2 database.

APPENDIX B. RESEARCH ARTICLES

B.1. Journal Publications

1. Stephen AJ, Archer SA, Orozco RL, and Macaskie LE: Advances and bottlenecks in microbial hydrogen production. *Microbial Biotechnology*. **10**. 2017. pp 1120-1127. DOI: 10.1111/1751-7915.12790

2. Archer SA, Murphy RJ, and Steinberger-Wilckens R: Methodological Analysis of Palm Oil Biodiesel Life Cycle Studies. *Sustainable and Renewable Energy Reviews*. **94**. 2018. pp 694-704. DOI: 10.1016/j.rser.2018.05.066

3. Archer SA and Steinberger-Wilckens R: Systematic Analysis of Biomass Derived Fuels for Fuel Cells. *International Journal of Hydrogen Energy***. 43**. 2018. pp 23178-23192. DOI: 10.1016.j.ijhydene.2018.10.161

B.2. Publications Under Review

1. Archer SA, Ingram A, and Steinberger-Wilckens R: Comparative Life Cycle Analysis of Biomass Derived Fuels for Fuel Cells. **In Review**.

APPENDIX C. CONFERENCE PROCEEDINGS

C.1. Oral

1. *An investigation into sustainable hydrogen pathways from biomass for fuel cells*. **Fuel Cell and Hydrogen Technical Conference 2015.** Birmingham, UK. 2015.

2. *Systematic review and life cycle analysis of different hydrogen production methods, their biomass feedstocks and SOFC applications*. **Fuel Cell and Hydrogen Technical Conference 2017.** Birmingham, UK. 2017.

3. *Systematic analysis of different hydrogen production methods, their biomass feedstocks and SOFC applications*. **The 7th World Hydrogen Technology Convention & Czech Hydrogen Days.** Prague, Czech Republic. 2017. (Updated results presentation).

C.2. Research Posters

1. *Application of LCA approaches to bio-based energy systems: A case study of palm oil biodiesel*. **Fuel Cell and Hydrogen Technical Conference 2015.** Birmingham, UK. 2015.

2. *Application of life cycle methodology to hydrogen from biomass*. **University of Birmingham Research Poster Conference**. Birmingham, UK. 2016.

3. *An investigation into sustainable hydrogen pathways from biomass for fuel cells*. **Fuel Cell and Hydrogen Technical Conference 2016.** Birmingham, UK. 2016.

4. *Assessment of sustainable hydrogen pathways from biomass*. **Czech Hydrogen Days**. Prague, Czech Republic. 2016. (Updated results poster).

5. *An investigation into sustainable hydrogen pathways from biomass for fuel cells*. **AEM 2016.** Guildford, UK. 2016. (Updated results poster).